Effect of Early Age Carbonation on Strength and pH of Concrete

by

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Abstract

Carbonation curing of concrete products has shown potentials for CO_2 capture and storage with environmental, technical and economical benefits in global greenhouse gas mitigation exercise. The primary objective of this study is to investigate the effect of early age carbonation on mechanical performance and pH of concrete in an attempt to understand the process and promote large scale applications.

It was found that significant early strength was developed in cement and concrete through early age carbonation curing. The early strength could be maintained and improved due to subsequent hydration. Twenty-eight-day strength of carbonated cement and concrete was comparable to that of hydrated reference if subsequently cured in the air in a sealed bag, but was lower if subsequently cured in water. Treatment with either internal curing using lightweight aggregates or chemical admixture can effectively enhance late strength development in carbonated concrete.

For three typical cement-based products including cement paste compacts, concrete compacts and precast concrete, two-hour carbonation reduced pH value from 12.8 to 11.8 as the lowest and subsequent 28-day hydration could slightly increase pH by 2% as maximum. At any time pH of early age carbonated concrete was always higher than 11.5, a threshold value under which the corrosion of reinforcing steel is likely to occur in concrete. The high pH in early-age carbonated concrete was likely attributed to the fact that early age carbonation was an accelerated hydration process, which was totally different from weathering carbonation in which pH of concrete could be neutralized due to the decomposition of calcium hydroxide and calcium silicate hydrates gel. Therefore, early age carbonation technology is applicable not only to concrete products such as masonry units and paving stones, but possibly to precast concrete with steel reinforcement as well.

Résumé

La cure de carbonatation de produits concrets a montré des potentiels pour la capture de CO_2 et le stockage avec des avantages environnementaux, techniques et économiques dans l'exercice de réduction de gaz à effet de serre global. L'objectif principal de cette étude est d'examiner l'effet de première carbonatation d'âge sur la performance mécanique et le pH de béton dans une tentative de comprendre le processus et promouvoir des applications de grande échelle.

Il a été trouvé que la première force significative a été développée dans le ciment et le béton par la première cure de carbonatation d'âge. La première force pourrait être maintenue et améliorée en raison de l'hydratation suivante. Vingt-huit force Jours de ciment gazeux et le béton était comparable avec celui de référence hydratée si par la suite guéri en air dans un sac scellé, mais était inférieure si par la suite guéri dans l'eau. Le traitement avec la cure interne utilisant des ensembles légers ou le mélange chimique peut efficacement augmenter le dernier développement de force dans le béton gazeux.

Pour trois produits à base de ciment typiques incluant la pâte de ciment rend compact, le béton rend compact et la carbonatation précontrainte concrète, de deux heures l'acidité réduite de 12.8 à 11.8 comme l'hydratation la plus basse et suivante de 28 jours pourrait légèrement augmenter le pH de 2% comme le maximum. À tout moment le pH de premier âge sous lequel le béton gazeux était toujours plus haut que 11.5, une valeur-seuil lequelle la corrosion de renforcer l'acier va probablement arriver dans le béton. Le haut pH dans l'âge premier le béton gazeux a été probablement attribué au fait qui vieillit tôt la carbonatation était un processus d'hydratation accéléré, qui différait totalement de la carbonatation de chasse d'eau dans laquelle le pH de béton pourrait être neutralisé en raison de la décomposition d'hydroxyde de calcium et le gel d'hydrates de silicate de calcium. Donc, tôt la technologie de carbonatation d'âge est applicable non seulement aux produits concrets comme des unités de maçonnerie et des pavés, mais probablement du béton précontraint avec le renfort d'acier aussi.

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Chapter 1 Introduction

1.1 General Overview

1.1.1 The Greenhouse Gas Effect

Greenhouse gas emission is believed to be responsible for climate change and global warming. The percentage contribution of major greenhouse gases is shown in Table 1.1. It is seen that carbon dioxide (CO_2) accounts for about 60% of greenhouse effect and is crucial to climate change.

Table 1. 1: Contribution of the major radiative gases affecting the earth-atmosphere energy (Modified from IPCC, 2001)

Gas	Radiative Forcing, Wm^{-2}	Effect on Earth-Atmosphere Energy Balance (%)
CO_2	1.46	60.2
CH_4	0.48	19.8
CFC_S	0.277	11.4
N_2O	0.15	6.2
CF_4	0.003	0.1
Others	0.055	2.4
Total	2.425	100

Greenhouse gas levels have significantly increased due to human activities since the beginning of industrial revolution. Changes in greenhouse gas levels, the rate of concentration and the atmosphere lifetime since pre-industrial times is shown in Table 1.2. Atmospheric concentrations of carbon dioxide have increased approximately 31% as high as pre-industrial levels. The current level of carbon dioxide is 365 ppm and it is rising at a rate of 1.5 ppm per year. (IPCC 2001)

It's widely accepted by scientists that greenhouse gases trap heat in the Earth's atmosphere and change in the global climate. By increasing the levels of greenhouse

gases in the atmosphere, human activities are strengthening Earth's natural greenhouse effect. The key greenhouse gases emitted by human activities remain in the atmosphere for periods ranging from decades to centuries. Worldwide mean surface temperatures have increased 0.3-0.6°C since the late 19th century. The 20th century's 10 warmest years all occurred in the last 15 years of the century. Sea level has risen 100-200 mm over the past century with approximately 66% of the rise coming from global warming (Miller 1998). Increasing concentrations of greenhouse gases are likely to accelerate the rate of climate change. Scientists expect that the average global surface temperature could raise 0.6-2.5 ° C in the next fifty years and 1.4-5.8 ° C in the next century, with significant regional variation. As the result, mean sea levels are expected to rise anywhere from 15 to 95 cm due to oceanic thermal expansion and glacial/ice-sheet melting (IPCC 1995). Moreover, global warming may increase the frequency and intensity of extreme weather events such as floods, droughts, heat waves, and hurricanes, change agricultural yields, cause glacier retreat, reduced summer streamflows, or contribute to biological extinctions.

Table 1. 2: Greenhouse gases affected by human activities (IPCC 2001)

	CO_2	CH_4	N_2O	CFC-11	HFC-23	CF_4
Pre-industrial Concentration	~280ppm	~700ppb	~270ppb	0	0	40ppt
Concentration in 1998	365ppm	1745ppb	314ppb	268ppt	14ppt	80ppt
Rate of Concentration Change	1.5ppm/yr	7.0ppb/yr	0.8ppb/yr	-1.4ppt/yr	0.55ppt/yr	1ppt/yr
Atmospheric Lifetime	5-200yr	12yr	114yr	45yr	260yr	>50000yr

*ppm - parts per million, ppb – parts per billion, ppt – parts per trillion

1.1.2 Sources of Carbon Dioxide

Currently, emissions from fossil fuel combustion have been identified as a significant source of anthropogenic CO_2. Roughly half of the anthropogenic emissions are absorbed into oceans and forests and the other half accumulates in the atmosphere. The

concentration of CO_2 has greatly increased from about 280 ppm in pre-industrial times to approximately 365 ppm in 1998. This increase can mainly be attributed to the fact that global emissions of CO_2 from human activity have increased from an insignificant level two centuries ago to 22.5 billion tons (Jaques *et al* 1997).

The global annual energy consumption by various energy sources for 1990 is shown in Table 1.3. Fossil fuels are the dominant form of energy utilized in the world (86%), and account for about 75% of current anthropogenic CO_2 emissions. The total amount of CO_2 emission was found to be 5.6 billion ton per year. Even though oil produced over 40% more energy than coal, they yielded very similar CO_2 emissions amount, which might be due to higher combusting efficiency of oil.

Table 1. 3: Global energy consumption and CO_2 emissions for various energy sources(1990) (Hellmann 1999)

Energy Source	Energy Produced (EJ^1/yr)	Total Energy Produced (%)	Carbon as CO_2 Produced, (Gt (C)/yr^2)	Total Carbon Produced (%)
Coal	91	23.7	2.3	40.4
Oil	128	33.2	2.4	42.7
Gas	71	18.4	0.9	16.9
Nuclear	19	4.9	-	-
Hydro	21	5.5	-	-
Biomass	55	14.3	-	-
Total	385	100.0	5.6	100.0

1 EJ = 10^{18} joules

2 Gt(C)/yr =10^6 tons of C as CO_2 per year

Source: IPCC 1996

The distribution of global CO_2 emission was presented in Table 1.4. It was showed that the power and industry sectors dominate current global CO_2 emissions, accounting for about 47% of total CO_2 emissions (1990). In the industrial sector, cement industry produced a relatively high concentrated CO_2 emission. It is estimated that the cement industry accounts for about 5% of global anthropogenic CO_2 emissions, equivalent to 1100 million tons of CO_2 (Worrell 2001).

Table 1. 4:Distribution of global CO_2 emission in 1990 (Halmann 1999)

Energy-Consuming Sector	Global CO_2 Emission (%)
Power and Heat Generation from Industry	47
Transportation	22
Commercial and Residential	31

1.1.3 International Policy

Over a decade ago, most countries joined an international treaty – the United Nations Framework Convention on Climate Change (UNFCCC), to begin to consider what can be done to reduce global warming and to deal with whatever temperature increases are inevitable. The Convention was the first binding international legal instrument providing a framework for addressing climate change issues. The Convention on Climate Change sets an overall framework for intergovernmental efforts to cope with the challenge posed by climate change. It recognizes that the climate system is a shared resource whose stability can be affected by industrial and other emissions of carbon dioxide and other greenhouse gases. Under the Convention, governments gather and share information on greenhouse gas emissions, national policies and best practices, initiate national strategies for addressing greenhouse gas emissions; and cooperate in preparing for adaptation to the impacts of climate change (http://unfccc.int/2860.php).

In December 1997, more than 160 nations met in Kyoto, Japan, to negotiate binding limitations on greenhouse gases. The outcome of the meeting was the Kyoto Protocol, which is the primary international agreement on combating climate change (http://www.eia.doe.gov/oiaf/kyoto/kyotorpt.html). Participating nations must reduce emissions for six major greenhouse gases, primarily carbon dioxide and must decide how to meet its respective reduction goal between 2008 and 2012. On December 17, 2002, Canada ratified the treaty, requiring it to reduce emissions to 6% below 1990 levels during these five years.

1.2 Strategies of Carbon Dioxide Storage

To stabilize the current CO_2 content in atmosphere and further reduce its emission, CO_2 capture and storage becomes necessary. Once carbon dioxide is captured and recovered from industries, there are several options for carbon dioxide disposal. These options include sequestration in ocean, depleted gas wells, active oil wells (enhanced oil recovery), coal beds and mines, salt domes, aquifers and natural minerals. Ocean disposal involves pumping carbon dioxide below the thermocline so that carbon dioxide can be readily dissolved. Adequate capacity of carbon dioxide dissolving can be provided by ocean to store all carbon dioxide from combustion of global fossil fuels resources. Depleted natural gas well is another feasible site for storage. However, they can only sequester carbon dioxide from combustion from natural gas with limited capacity because one volume of natural gas combustion produces one volume of carbon dioxide. Another means for carbon dioxide storage is active oil wells. It is to use carbon dioxide to remove a substantial portion of oil remaining after primary oil production removes one third of oil. Only limited fraction of carbon dioxide can be stored through oil combustion in wells since volume of compressed carbon dioxide gas is much greater than that of liquid oil (Halmann 1999). One of these options is under investigation for purpose of carbon dioxide storage in coal mines and deep beds. Carbon dioxide is supposed to be injected into coal deposits and displace the natural gas. Solution-mines salt domes are also possibly applied to sequester carbon dioxide gas. Approach of deep aquifer storage of carbon dioxide has been practiced in some projects in Norway and Indonesia. It is also indicated that a great capacity for carbon dioxide storage is possible in U.S. aquifers. Several projects have been currently in progress using sequestration approaches. In Weyburn, Saskatchewan, CO_2 transmitted from North Dakota to Weyburn is applied to enhance oil recovery, storing 14 million tons of CO_2 over 15-20 years (Mourtis 2003). In New Mexico, for the West Pearl Queen project, 2200 tons of CO_2 will be injected into a depleted oil field over 42 days. Projects in New Mexico are expected to take 280,000 tons of CO_2 over 6 years and Virginia project will take 26,000 tons of CO_2 over 1 year, using an unmined coal seam (NETL 2004).

Ingeous rocks containing magnesium oxide bound to silica and alumina-forming aluminosilicates are the last candidate for carbon dioxide sequestration. Mineral carbonation has been developed to produce stable carbonates by reacting carbon dioxide with magnesium silicate minerals such as olivine and serpentine. Estimates reveal that there exists a large amount of these natural minerals, far exceeding the known fossil fuel reserves (Lackner *et al* 1995). Although carbonation reaction efficiency was found to be about 60-80%, it is inherently expensive. Therefore, investigation is being conducted to make improvement to achieve technical and economical benefits (Penner *et al* 2004).

1.3 Carbon Dioxide Storage in Cement and Concrete Building Products

Another approach of CO_2 storage has been examined at McGill University using calcium silicate building products to convert CO_2 to calcium carbonate. The reaction of hydraulic and non-hydraulic calcium silicates with CO_2 were comprehensively investigated by some researchers (Berger *et al* 1972, Young *et al* 1974, Goodbrake *et al* 1978, Bukowski and Berger 1979). This process is called carbonation curing. It is an accelerated process that injects carbon dioxide gas into curing vessel at room temperature, diffuses carbon dioxide into the calcium silicates, and transforms carbon dioxide into solid calcium carbonates. Generally, this process occurs at a high CO_2 pressure and concentration, generating a rapid and exothermic reaction. The products after complete carbonation are primarily calcium carbonates and silica gel. The chemical reactions are given as follows:

$$3CaO{\cdot}SiO_2 + 3CO_2 + \mu H_2O \rightarrow SiO_2{\cdot}\ \mu H_2O + 3CaCO_3 \quad (1.1)$$

$$2CaO{\cdot}SiO_2 + 2CO_2 + \mu H_2O \rightarrow SiO_2{\cdot}\ \mu H_2O + 2CaCO_3 \quad (1.2)$$

Based on previous assumption proposed by Bukowiski and Berger (1974), Berger *et al* (1972) and Moorehead (1986), and cited by Qi (2005), this complex process can be described to proceed in a sequence of steps given below:

1. Dissolution of carbon dioxide gas in water to form carbonic acid.
2. Interaction of CO_3^{2-} and Ca^{2+} to form highly insoluble calcium carbonate, which coats cement particles and then precipitates to fill the larger pores .

3. Diffusion of CO_3^{2-} to the reaction zone through the dense carbonated outer surface.
4. Reaction continues until CO_3^{2-} or Ca^{2+} is depleted or no water exists in the system.

The Steinour formula (Steinour 1959) estimates the theoretical maximum CO_2 uptake by Portland cement concrete based on the chemical composition of cement binder using the following equation:

$$CO_2(\%) = 0.785(CaO - 0.7SO_3) + 1.091MgO + 1.420Na_2O + 0.935K_2O \quad (1.3)$$

This formula would suggest that the maximum CO_2 uptake for Portland cement of typical composition of 63% CaO is approximately 50%. Put it another way, assuming 100% carbonation degree, one tone of cement would absorb a half ton of CO_2. This efficiency means that CO_2 emitted from decomposition of limestone during cement production can be totally sequestered into concrete products.

Carbonation curing differs from weathering carbonation that naturally occurs in matured concrete. Weathering carbonation has been extensively studied in past several decades. It refers to reaction of hydrated compounds in hardened concrete with atmospheric carbon dioxide over a long period of time. The major chemical reactions of weathering carbonation are present in equations 1.4 and 1.5. Weathering carbonation becomes a concern in reinforced concrete as a result of pH reduction in pore solution, which may initiate corrosion of reinforcing steel.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (1.4)$$

$$3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3CO_2 \rightarrow 3CaCO_3 + 2SiO_2{\cdot}\,3H_2O \quad (1.5)$$

Partial hydration prior to carbonation curing will result in reaction between carbon dioxide gas with both hydrated compounds and anhydrated phases. As a result, two series of chemical reactions in Equation 1.1-1.2 and 1.4-1.5 may occur simultaneously.

Not only can cement and concrete products be used to reduce greenhouse effect, the approach of carbonation curing possesses some technical benefits as well as with

enhanced performance. The rapid reaction between carbon dioxide and anhydrated phase can result in higher early-age strength than that of conventional hydration. Production can thus be accelerated with less time to achieve green strength. Accelerated hardening of cement-based products with carbon dioxide is being systematically investigated at McGill University. Absorption of carbon dioxide has been studied in several different cement-based building products, including cement board, concrete blocks, and fibre-cement board. With the increasing demand of cement-based building products, carbonation curing technology provides a viable approach for carbon dioxide storage. Furthermore, with certain amount of carbon dioxide uptake, cement-based products can achieve better properties with respect to strength and durability. For commercial application, concrete production facilities can be located next to cement plant or power plant where the flue gas from plants can be pumped directly to the curing chamber for carbonation curing of cementitious products and for carbon dioxide storage.

To investigate the environmental and technical benefits of carbonation technology for carbon dioxide storage and product development, a systematic study has been carried out at McGill University to understand the carbonation process, the CO_2 storage capacity of different calcium-carrying materials and the influence of process parameters.

Most previous work has been done focusing on mechanical performance of products immediately after carbonation curing (Chad 2006, Wang 2007). In fact, the final mechanical performance of carbonated cement-based products is not only dependent on early age carbonation curing but also on the subsequent hydration. Systematic investigation should thus be performed to examine if rapidly developed early-age strength can be maintained or improved through subsequent hydration after carbonation treatment. Based on previous research at McGill University, water loss was found to be significant through carbonation curing on both cement paste and concrete compacts (Chad 2006). This might lead to insufficient hydration of carbonated products due to very low water cement ratio after carbonation reaction. Thereafter, concept of internal curing is applied in this project to compensate for the water shortage in carbonated cementitious products so that at later age the mechanical properties can be improved.

This carbonation curing technology was suggested to be suitable for concrete products without reinforcing steel because there is a concern that carbonation process reduces pH of pore solution and initiates reinforcement corrosion in hardened concrete. It was suggested that CO_2 lowers the pH of the pore fluid through early age CO_2 treatment (Berger *et al* 1972), however quantification of its reduction was not reported. It therefore becomes a concern whether the pH will be reduced or not, and how much it will be decreased through early age carbonation curing.

Gas pressure is a crucial parameter during carbonation curing process. It should be intentionally kept low to make the process practically feasible. Moreover, application of CO_2 gas pressure is related to energy consumption. Gas pressure of 0.5 MPa was applied in the previous researches at McGill University (Chad 2006, Wang 2007). It is thus necessary to examine if lower gas pressure can achieve the same net gain in CO_2 storage as that obtained under higher pressure.

1.4 Research Objectives

The objectives of this research are three-fold:

1. To investigate 28-day mechanical performance of carbonated cement-based products and understand the mechanism of strength change during subsequent hydration process.
2. To quantify pH value of carbonated cement-based products immediately after carbonation treatment as well as after subsequent 28-day hydration; and to examine correlation between CO_2 uptake and the pH.
3. To study the effect of gas pressure of 0.15 MPa on carbonation curing characteristics and mechanical performance as well as the pH of carbonated cementitious products.

The following tasks will be carried out to achieve aforementioned objectives in this research work:

1. Characterization of carbonation behaviour of cement paste compacts, concrete compacts and precast concrete in terms of peak temperature, water loss and carbon dioxide uptake.
2. Quantification of carbon dioxide content during carbonation curing through weight gain method, mass curve method and constant-temperature pyrolysis techniques.
3. Evaluation of strengths of carbonated products after carbonation curing and subsequent hydration up to 28 days.
4. Development of an innovative approach using internal curing agent and chemical admixture to compensate for water loss caused by carbonation reaction.
5. Assessment of phenolphthalein method for carbonation depth in carbonated products.
6. Phase analysis by x-ray diffraction (XRD) method.
7. Measurement of pH of pore solution in carbonated products after carbonation curing and subsequent hydration up to 28 days.
8. Carbonation curing on precast concrete with high water to cement ratio and pre-drying.
9. Investigation into carbonation behaviour, mechanical performance as well as the pH of carbonated precast concrete after carbonation curing and subsequent 28 day hydration.

A comprehensive literature review will be summarized in Chapter 2. Experimental program is presented in detail in Chapter 3. Chapter 4 discusses the experimental results. Three typical cement-based products — cement paste compact, concrete compact and precast reinforced concrete are respectively discussed in three subsections. Finally, a summary of conclusions and recommendations for future work are proposed in chapter 5. All experimental data are shown in Appendices at the end of the thesis.

Chapter 2 Literature Review

This chapter provides a comprehensive review on reaction mechanism of carbonation curing of cement and concrete and their strength development immediately after carbonation as well as after subsequent hydration. The concept of internal curing is also reviewed as a tool to compensate for the water loss during carbonation reaction and improve hydration after carbonation treatment. Studies on the pH reduction of pore solution in hardened concrete due to carbonation are summarized.

2.1 Carbonation Curing

2.1.1 Reaction Mechanism

Accelerated curing of fresh Portland cement using carbon dioxide is achieved through the rapid hydration of calcium silicates to a combination of calcium-silicate-hydrates (CSH) and calcium carbonates ($CaCO_3$). Using tricalcium silicate (C_3S) and dicalcium silicate (C_2S) mortar compacts, it was found that carbonation reaction was extremely rapid during the first 10 minutes (Young *et al,* 1974). The initial reaction with carbon dioxide accelerated hydration of C_3S, forming $CaCO_3$ and CSH. For C_3S compacts, the amount of C_3S reacted within 3 minutes and that in 12 hour normal hydration were on the same order with comparable stoichiometry. Thereafter, reactions progressed mainly between carbon dioxide and CSH. As the reaction continued, CSH produced through hydration was rapidly carbonated. Equation 2.1 shows the initial reaction forming calcium carbonate and CSH, where x depends on the degree of carbonation (Young *et al* 1974). It was suggested that CSH in the equation 2.1 was short lived as it could be reacted with carbon dioxide to form calcium carbonated and silica gel, as described by Equation 2.2 (Goodbrake *et al* 1979).

$$C_nS + (n-x)\overline{C} + yH \rightarrow C_xSH_y + (n-x)C\overline{C} \quad (2.1)$$

$$C_nS + n\overline{C} + zH \rightarrow SH_z + nC\overline{C} \quad (2.2)$$

Cement nomenclature is used throughout: C – CaO; S – SiO_2; H – H_2O; $\overline{C}$ – CO_2

X-ray diffraction (XRD) analysis of the carbonated C_3S compacts after 81 minutes indicated that calcite was the only crystalline carbonate, showing no evidence of other carbonated compounds (Young *et al* 1974). Aragonite was suggested to form when the system is allowed to dry out (Goodbrake *et al*, 1979). Moreover, it was found that both calcite and vaterite were formed during the carbonation of C_2S mortars (Bukowski and Berger 1979). Previous work completed by Cole and Kroone (1960) and Sauman in 1971, as cited by Young *et al* (1974), detected both aragonite and vaterite in carbonated CSH gel. It was argued that an amorphous calcium silicate hydrocarbonate might be produced during carbonation of C_3S and C_2S besides calcium carbonate (Goto *et al* 1995). The formation of calcium carbonate has been proved by XRD or thermal analysis by other researches, and the formation of CSH and calcium silicate hydrocarbonate have not been verified yet.

Water is prerequisite for the dissolution of carbon dioxide to form carbonic acid, which subsequently dissolves calcium ions to form highly insoluble calcium carbonate. However, excessive water inhibits the carbonation reaction by saturation of pores that influence diffusion of carbon dioxide. Evolution of high heat caused the core material of sample to remain largely unreacted due to insufficient water (Young *et al* 1974). Water starvation has been understood to be a limiting factor in carbonation reaction. It has been proposed that, for compacts with low water to cement ratio, water loss can restrict the potential reaction to approximately 25% of the maximum (Berger *et al* 1972).

2.1.2 Compressive Strength Development

Compared with conventional hydration, strength development through carbonation curing was rapid. The amount of C_3S reacted after three minutes was similar to that after 12 hour normal hydration (Young *et al* 1974). Strength gain in C_2S compacts could be compared to that of C_3S when disregarding the somewhat slow reaction at early stage. While there appeared to be a correlation between the amount of C_3S carbonated and the compressive

strength, the compressive strength was dependent on the quantity of carbon dioxide uptake. In later reaction from 27 to 81 minutes, the strength continued to increase without additional reaction in C_3S. This suggested that carbonation of CSH accounted for strength gain in later reaction (Young *et al*, 1974). Other research using both C_3S and Portland cement mortars found that after 5 minute injection strengths were approximately similar to those after 1 day conventional hydration (Bukowski and Berger 1979). Despite of prolonged carbonation, the core of cement specimens remained largely unreacted and strength gain was not apparent any more. Subsequent moist curing of carbonated samples provided additional strength, paralleling that of conventional hydration (Young *et al* 1974).

Conflicting results were also reported on long term strength of carbonated cement-based products. A study was conducted on whether subsequent hydration after carbonation would significantly improve strength (Klemm and Berger 1972). Type II mortars (sand:cement:water =1:1:0.12) were compacted at about 5.9 MPa, treated with CO_2 at a gas pressure about 0.4 MPa for 5 minutes, then stored in sealed plastic bags for 18 hours and placed under water. The strengths of carbonated and non-carbonated samples were tested at ages of 1, 3, 7 and 14 days. Immediately carbonated samples possessed higher compressive strength than that of samples hydrated for 1 day. The strength improvement was observed to be 30% in 1 day and the strength slightly exceeded that of sample normally hydrated for 7 days. After this initial development, a strength plateau was observed in carbonated samples after 3 days up to 2 weeks. Although strength of carbonated samples were somewhat developed in subsequent hydration, it did not catch up with that of conventionally hydrated samples at same age. It was suggested that this might have occurred due to the following possibilities: 1) subsequent hydration was hindered or ceased by early age carbonation curing; 2) cement-based products in post carbonation-hydration process might be weaker than those conventionally hydrated.

Compressive strength development in carbonation-hydration process was investigated on Portland cement mortar samples (Hannawayya 1984). Vacuum carbonation method was applied on cement mortar specimens (sand:cement:water =3:1:1) with a compaction

pressure of about 2.9 MPa. It was observed that the compressive strength of 48.2 MPa was achieved by 38 minute carbonation and exceeded those developed under 28 day normal hydration in air. However this carbonation curing led to compressive strength decreased to 28.6 MPa after carbonation followed by 28-day air curing and reduced to 36.1 MPa after 7 day curing in water and up to 28 days in air. Conversely, hydrated mortars had relative low initial compressive strength, continued to gain strength and exceeded strength of carbonated samples at 28 days. It was therefore proposed that the cement-based products in carbonation-hydration process were inherently weaker than that developed in normal hydration.

Decrease of long-term compressive strength through carbonation reaction of sodium carbonate (Na_2CO_3) modified cement paste was reported by Janotka (2001). Sodium carbonate is categorized as an accelerating admixture mainly influencing the acceleration of tricalcium silicate (C_3S) hydration. It was proposed that reduced long-term compressive strength could be attributed to the loss of binding capacity, which resulted from preferential built-up of calcium carbonate ($CaCO_3$) formed on the surface of cement grains at early-age of cement hydration. The larger amount of non-affected products of hydration by the action of CO_2, the better compressive strength the cement paste would become in the long term.

2.2 Concept of Internal Curing

It was recognized that the long-term strength reduction in cement paste and mortar might be attributed to the loss of binding capacity and loss of water during carbonation process. Both of these two losses can be compensated by the introduction of additional moisture in to cement phase to improve the later strength. Internal curing is an effective approach to achieve this goal.

Internal curing was developed nearly 16 years ago by Philleo (1991), who suggested incorporating saturated lightweight fine aggregate into the concrete to provide an internal source of water necessary to replace that consumed by chemical reactions during

hydration. This novel approach is known as internal or autogenous curing, which can mitigate self-desiccation of high performance concrete. A certain amount of pre-soaked lightweight aggregates (LWA) has been applied for high performance concrete with low water to cement ratio to ensure sufficient hydration. These pre-wetted LWA particles are uniformly distributed throughout the cementitious matrix to act as an internal water reservoir. Theoretically, when water starvation occurs in the cement paste, water from pre-soaked LWA will be transported to the drier cement paste regions, where the reaction with anhydrated phase may advance (Weber and Reinhardt 1997, Bentur *et al* 2001). With further hydration of cement and increase in density of the structure, the transport of water slows down and eventually ceases when the relative humidity in the LWA particle and in the hardened matrix are in equilibrium (Jozwiak-Niedzwiedzka 2005). Although the function of internal curing has been observed for many years, some fundamental questions about mechanism of internal curing are not yet well understood.

Most of work that has been done is to eliminate autogenously shrinkage (Benz and Snyder 1999, Zhutovsky *et al* 2004, Kovler *et al* 2004, Lura 2005) or improve the scaling resistance (Jozwiak-Niedzwiedzka 2005) while using smallest possible amount of weaker LWA. Herein, effect of internal curing on strength improvement is more concerned. Most of the researches focus on compressive strength of concrete incorporating pre-soaked LWA. Although the introduction of pre-wetted LWA had an effect on early strength, the strength greatly increased in further hydration and could be close to or even exceed their reference without soaked LWA at later ages, which might be promoted by extra water supplied by LWA (Zhutovsky *et al* 2004, Lura 2005).

2.3 Carbonation-induced Corrosion

2.3.1 Chemical Process of Carbonation on Hardened Concrete

Carbonation of matured concrete has been extensively studied to understand the mechanism of carbonation-initiated corrosion and to develop measures to prevent it from happening. It is stated that what is measured and relevant is the pH of the liquid phase in

equilibrium with the matured concrete. The pore solution in equilibrium with non-carbonated concrete generally has a pH which is 12.5-13.5 due to the dissolved calcium hydroxide and alkali content in cement. Comprehensive study has been conducted on carbonation of reinforced concrete, including the causes, influences and management strategies. A review was given by Richardson (1988). The Pore solution plays an important role in carbonation phenomenon. It is the pH of pore solution phase that reflects the essential change in chemical composition of concrete. Generally for matured concrete, carbon dioxide reacts with almost all phases of hydration products principally including calcium hydroxide. While the role of calcium hydroxide is predominant, other hydrated cement compounds also are involved. The mechanism of this reaction requires the dissolution of carbon dioxide gas in the pore solution and involves the formation of a weak carbonic acid which dissociates into hydrogen and carbonate ions. For fresh concrete, it is more important to consider effect of carbonation on anhydrated phase. It is stated that carbon dioxide lowers the pH of the pore water through the formation of carbonic acid which is neutralized by the calcium silicates which leads to the precipitation of highly insoluble calcium carbonate (Berger *et al* 1972). The ingress and reaction of carbon dioxide causes the pH to fall resulting in partial and subsequent carbonation of calcium silicate.

2.3.2 Threshold pH Value to Initiate Corrosion of Steel in Reinforced Concrete

The pore solution in concrete normally attains an alkaline level with the pH greater than 12.5. In this alkaline liquid phase a thin oxide film forms on reinforcement surface which protects the embedded steel. The integrity and protective quality of this film depend on the level of alkalinity. The effectiveness of this passivating film on a steel surface is a function of the pH of the pore solution around the metal (Richardson 1988). The alkaline environment will safeguard the protective film as long as the pH of surrounding solution remains within certain limits. It might be argued that to assess the likelihood of reinforcement corrosion it is necessary only to detect regions where the pH is less than

9.0 (Parrott *et al* 1989). In fact, if the pH of concrete drops below 9, the protective oxide film on the steel surface will be completely impaired (CEB 1988).

Efforts have been made in last 50 years to determine the threshold pH value, under which reinforcement corrosion is likely to occur. The behaviour of steel in concrete or mortar was well understood by a study of submerged corrosion of steel in alkaline solutions (Shalon and Raphael 1959). It was proposed that if the pH exceeded 11.5, and certain ions, such as Cl^- was absent, a passivating film on the steel was normally maintained. It was therefore indicated that pH = 11.5 might be considered sufficient to inhibit corrosion of steel. An independent investigation was also conducted on corrosion behaviour of reinforcing steel in simple alkaline solutions of different pH (Gouda 1970). It was estimated that the critical pH value, above which stable passivity occurred, was 11.5. This threshold pH value of 11.5 was widely accepted by most of researchers who were working on carbonation corrosion, including evaluating the corrosion hazard for carbonated concrete (Gjørv 1982, Krajči and Janotka 2000, Chang *et al* 2004).

2.3.3 pH Assessment Method

A commonly used method to measure pH of concrete is to press pore solution from concrete and analyze the extracted liquid. A device with high pressure up to a few hundreds MPa has been used for pore solution expression from hardened Portland mortars with water to cement ratio of 0.5. (Barneyback and Diamond 1981). This device employs an operating pressure of the order of 550MPa applied to roughly 250g sample of hardened mortar to completely fracture the specimen. Such mortars yielded typically 10 ml of pore fluid shortly after set but only 1 or 2 ml might be extracted after a long period of hydration. Instead of using pH electrodes, OH^- was determined by direct titration against standard HCl. Similar device was also employed for the study on the relation between pore fluid characteristics and expansion due to alkali silica reaction (ASR) (Durand *et al* 1990). The pore solution extraction technique consisted of pressing a confined sample with sufficient pressure to express the contained liquid. The apparatus was made of two parts: the pressure chamber and the collecting system. Approximate

300MPa by means of hydraulic press was utilized. Both pH electrode measurement and titration method were proposed for analyzing extracted pore fluid. However, the latter approach was preferred because it was difficult to use pH meter to measure small amount of pore solution available. As a result, OH^- ion concentrations were obtained by titration with an H_2SO_4 solution using phenolphathalein solution as indicator. To investigate effect of carbonation on corrosion-related properties, carbonated cement paste discs (water: cement=0.6) with saturated surface dry, were subjected to pore solution expression by means of a similar device at a pressure up to 300MPa (Anstice and Page 2005). The extracted pore solution was analyzed by both pH electrode measurement and titration. The carbonated samples under different CO_2 concentration all yielded pore solution with pH less than 11.0.

Although this method is well documented and a number of studies have been reported in which the method has been tested and solutions have been analyzed, extracting the fluid under high pressure from the pores of hardened concrete is very difficult, especially with samples of low water to cement ratio. A simple method was proposed to determine the pH value of pore solution in concrete and fine smoothing mortars. It can also be applied for the studies of carbonation corrosion and alkali silica reaction (Räsänen and Penttala 2004). This proposed suspension method is based on mixing powder sample with distilled water and measuring pH of the suspension solution. Investigation was conducted on main parameters affecting the measurement results involving solvent/solid ratio, fineness of pulverized sample, stirring time, extraction time, filtration and temperature of powder and solvent. In their laboratory work, some 30g samples were pulverized. Amount of powder and distilled water with various solvent/solid ratios were then mixed for 30 seconds up to 120 minutes and allowed to settle from 1 minute to 1 week. It was found that the higher the portion of concrete powder the greater the pH of the suspension solution. The difference in the ratio of powder to water content used to prepare aqueous solution was not likely to alter the results from civil engineering point of view (Rajamane and Sabitha 2005). The results also indicated that the pH of the suspension solution increased with increasing fineness of concrete particle size, stirring time and extraction time. Filtration before measurement did not decrease pH values noticably. Its validity was also

investigated by comparing pH results obtained from suspension method with those of the extracted pore water by high-pressure compression setup. No remarkable discrepancies could be observed between suspension method and extraction method through a device with high pressure. It was found that the pH value of concrete was 12.84±0.03 using suspension method without filtration before measurement with electrode. And the pH value of the same suspension solution was 13.16±0.05 using extraction method by use of high pressure device. In this thesis, pH of pore solution phase in cement-based products will be measured using suspension method with appropriate parameters, which will be presented in detail in section 3.4.6.

2.3.4 pH of Pore Solution in Carbonated Cement-Based Products

2.3.4.1 Carbonation of Hardened Cement and Concrete

Carbonation of matured concrete was extensively investigated because of the concern for its durability. The attention is primarily paid to the reduced pH which might lead to corrosion of the steel reinforcement. The carbonation reaction can reduce the pH value of the pore solution in concrete ranging from 12.5 to 13.5 to a value of about 8.3 if it is totally carbonated (Richardson, 1988). This causes the passive layer that usually covers and protects the reinforcing steel against corrosion to be destroyed (Neville 1995). A number of laboratory studies have been conducted to investigate pH of pore solution phase in carbonated cement paste and concrete to examine carbonation-induced corrosion.

Jerga (2004) studied influence of carbonation on physico-mechanical properties of hardened concrete. Four groups of concrete samples were prepared with different water to cement ratio ranging from 0.47 to 0.80 and various methods of curing. Prior to carbonation treatment, the specimens were placed in moist chamber and in air for hydration by 8 and 175 days. For particular series, curing conditions were simulated by drying samples at 65°C for 4 days at the age of 3 days. Thereafter, accelerated carbonation experiment was carried out for several months in sealed vessels with the CO_2 concentration of 15% and the pressure up to 1MPa. A set of four solution indicators were applied on the fresh fracture surface of the concrete to present the progress of carbonation

with pH values. It was observed that the specimens treated with CO_2 at enhanced concentration achieved high carbonation degree with pH value less than 8, while non-carbonated samples with normal method of curing had pH values greater than 11.5.

Research had been conducted on pore fluid analysis of cement pastes to predict effect of carbonation on corrosion-related behavior of concrete (Anstice *et al* 2005). Matured cement paste specimens of water to cement ratio 0.6 were prepared with curing in saturated air for 2 weeks and then at 38°C for 12 weeks after remolding. They were then cut to 5mm-thick discs for carbonation with various concentrations of CO_2: 100%, 5% and 0.03%. The pore solution was then pressed by a device with high pressure up to 300 MPa. pH values of pore solution extracted from non-carbonated samples was observed to be 13.49; while the carbonated samples of the same composition under different concentration all yielded pore water with PH less than 11.0. It was also found that the higher the concentration of CO_2, the more complete neutralization in the pore fluid. For samples treated under CO_2 concentration of 100%, pH was found to be 7.1 by the lowest.

During investigation of concrete carbonation depth, three zones of carbonation were determined by degree of carbonation and the respective pH of pore solution (Chang and Chen 2006). Concrete cylinders with water to cement ratio of 0.65 were cured for 28 days. Thereafter, they were subjected to accelerated carbonation at 23°C 70% RH and 20% concentration of carbon dioxide gas for 8 and 16 weeks. Suspension solution was prepared with mixing pulverized concrete powder sized 2-5mm with water in a solid to liquid ratio of 0.1. The mixture was placed in a sealed container under 15°C for 20 days and filtered before measurement. pH in the pore solution was measured using a pH electrode. It was proposed that the pH of the pore solution in concrete changed with carbonation degree. For non-carbonated zone, the pH of pore solution was found to be greater than 11.5, while the pH value dropped between 9.0 and 11.5 for partially carbonated region with carbonation degree between 0% and 50%. When degree of carbonation exceeded 50%, the pH value was between 7.5 and 9.0. Once full carbonation was achieved, the pH in the pore solution was smaller than 7.5.

2.3.4.2 Carbonation of Fresh Cement-based Products

It is well accepted that carbonation of matured concrete causes pH value of pore solution to decrease leading to loss of passive film and corrosion protection for steel in reinforced concrete. pH value of pore water phase will drop below 9.0, if the hardened concrete has been totally carbonated (CEB 1988). It was suggested that early age carbon dioxide treatment also decreased pH of pore solution through the formation of carbonic acid which in turn was rapidly neutralized by leaching of Ca^{2+} from calcium silicates, leading to the immediate precipitation of insoluble calcium carbonate (Berger *et al* 1972). Based on this understanding, application of early-age carbonation is only confined to non-steel reinforced products. However, seldom work has been done to quantify pH reduction of pore solution initiated by early-age carbonation.

Properties of carbonated products were examined right after carbon dioxide injection and 28 day curing in order to investigate application of carbonation curing on accelerated hardening of wood-cement composites (Qi 2005). After carbon dioxide treatment, carbonated samples were cured in sealed bags for 28 days and the pH of pore solution was assessed. Suspension solutions were obtained by mixing crushed samples with distilled water (solid:water =3) and allowing to stand about 1 hour. Thereafter, pH values were measured using pH meter at about 22°C. It was observed that pH values in carbonated wood-cement composites were still very high and decreased with injection time. After 30 minutes of carbon dioxide injection, wood-cement composites had a 28 day pH value of 11.7, much higher than usually assumed level around 9.0. It was suggested that the result could be explained by the fact that approximate 66% of the calcium oxide remained unreacted in the composites immediately after 30 minute carbon dioxide treatment.

Chapter 3 Experimental Program

Three typical cement-based building products, such as cement paste compacts, concrete compacts and precast concrete samples with reinforcement, were investigated for their early-age carbonation behaviour, strength development and pH values.

Cement paste compacts were initially tested to investigate the gas pressure effect on characteristics of carbonation curing such as peak temperature, water loss and carbon dioxide uptake. Mechanical behaviour, pH value, carbonation depth and X-ray diffraction were performed immediately after carbonation as well as after subsequent hydration of 28 days in different curing conditions. The effect of carbonation time was also investigated on fresh cement paste compacts.

Concrete compacts were prepared following the industry process of masonry blocks and paving stones. Concrete samples were examined in terms of carbonation curing characteristics as aforementioned, strength development and pH change right after carbonation treatment and after following 28-day hydration.

Preliminary feasibility study was conducted on carbonation curing of precast concrete. Presetting and drying process was monitored prior to treatment with carbon dioxide. Carbonation curing behaviour of precast concrete was determined by peak temperature, water loss and mass gain. Compressive strength, qualitative depth of carbonation and X-ray diffraction testing were also conducted after carbonation and subsequent hydration up to 28 days. The purpose of pH measurement herein was to investigate if early age carbonation reduced pH of concrete below the threshold value of 11.5.

3.1 Carbonation Curing Setup

The carbonation curing setup was developed to treat fresh cement paste and concrete compacts as well as preset precast concrete with a high concentration of carbon dioxide gas at two gas pressure of 0.15 MPa and 0.5 MPa. The apparatus is composed of carbon

dioxide gas tank, pressure vessel, thermocouple, pressure transducer, in-situ electric balance and data acquisition system. The schematic of carbonation curing apparatus is shown in Figure 3.1. The major components are briefly described as follows.

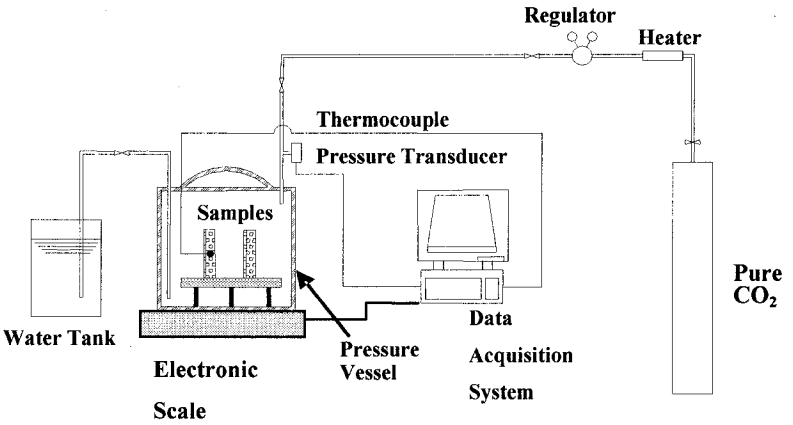


Figure 3. 1: Carbonation curing setup

3.1.1 Compressed Carbon Dioxide Gas Tank and Fittings

Carbon dioxide gas used in this project was in a compressed liquid/gas state manufactured by a local distributor (Megs Inc.). The cylinder of a size 1A contained 27.22kg of carbon dioxide gas with a purity of 99.8%. A Model 425-125-320 Harris Calorific Inc. single stage regulator was fitted in the gas tank to moderate the gas pressure from the tank to the pressure vessel. The regulator was fitted with two pressure gauges to monitor the tank pressure and outlet pressure respectively. The tank pressure gauge had a range from 0 to 28 MPa with a precision of 1 MPa, while the outlet gauge had a pressure range from 0 to 1.4 MPa with a precision of 0.05 MPa. These regulators were used in gas delivery system to reduce high-pressure gas to the desired pressure level and maintain it during carbonation curing by adjusting this regulator. The carbon dioxide gas existed at a temperature much cooler than room temperature because it was in a highly compressed liquid/gas state in the cylinder. Therefore, an electric heater was attached between the tank and regulator to heat the carbon dioxide as it exited the tank. The heater was

manufactured by Matheson and thermostatically controlled to prevent overheating of the gas.

3.1.2 Pressure Vessel

The pressure vessel for carbonation curing is manufactured by Alloy Products Corp with a volume of 5.5 litres and a pressure capacity of about 1 MPa. For three groups of specimens used in this project, depth varies from about 14mm to 30mm with constant length and width (127mm by 76mm). The maximum number of specimens that can be accommodated in pressure vessel at the same time was six. The curing chamber was equipped with a steel plate used as a base to support samples and a lid fitted with a rubber O-ring seal as well as some outflow tube assemblies with a pressure resistance capacity of about 2 MPa.

3.1.3 Thermocouple and Pressure Transducer

A thermocouple was attached in the pressure vessel to monitor the temperature change on specimen surface during carbonation reaction. A type T copper/constant thermocouple with superior corrosion resistance was connected with the data acquisition system to record the surface temperature of the sample. One pressure transducer with a capacity of 0.7 MPa was installed in conjunction with the data acquisition system to monitor the gas pressure in the chamber during carbonation curing process.

3.1.4 In-situ Ohaus Digital Balance System

To record instantaneous mass change of the entire close system during carbonation curing, an in-situ Ohaus balance was used along with its own data acquisition system. The electrical scale has a weighing capacity of 20kg with a precision of 2g. The interval of mass recoding during carbonation curing was specified to be 30 seconds. This system is also applied to monitor water evaporation of precast concrete samples during presetting process with specified intervals of 10 minutes.

When air was injected into curing vessel with gradual pressure levels from 0.138MPa (20 psi) to 0.552MPa (80 psi), the gas mass was recorded by both an electrical scale with an accuracy of 0.1g and in-situ Ohaus balance system. The mass of air in vessel under different pressure levels were measured respectively for three cement-based samples due to different volume of tested samples. The mass-pressure curve recorded for cement paste compacts is displayed in Figure 3.2. The linear relationship between air pressure and mass are summarized in Table 3.1. The mass of air and pure CO_2 gas in curing vessel under pressure of 0.5 MPa and 0.15MPa can be calculated from this correlation and all results are shown in Table 3.2. These data will be used to calculate residual mass of CO_2 gas in the curing vessel for mass curve correction.

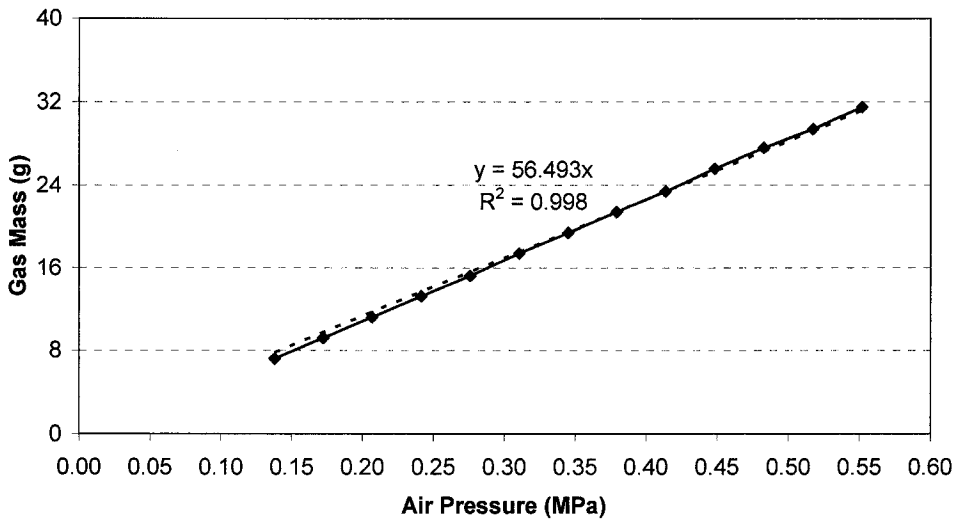


Figure 3. 2: Mass of air in curing vessel under different pressure levels for carbonation of six cement paste compacts

Table 3. 1: Correlation of air pressure and mass in curing vessel

Batch Description	Linear Correlation Between Air Pressure(x) and Mass(y)	R^2
Six Cement Paste Compacts	y=56.493x	0.998
Six Concrete Compacts	y=54.488x	0.995
Six Precast Concrete samples	y=51.053x	0.996

Table 3. 2: Mass of air and CO_2 in curing vessel under different pressure

Batch	Gas Pressure (MPa)	Mass of Air(g)	Mass of CO_2 Gas (g)*
Six Cement Paste Compact	0.50	28.2	42.8
	0.15	8.5	12.9
Six Concrete Compact	0.15	8.2	12.4
Six Precast Concrete Samples	0.15	7.7	11.7

Mass of CO_2 Gas (g)*= mass of air (g) × (molar mass of CO_2÷molar mass of air)
Where, molar mass of CO_2=44g/mol and molar mass of air=29g/mol

3.1.5 Data Acquisition System

The data acquisition system, a product of Measurement Groups Inc 5100 scanner, was used in conjunction with the thermocouple and pressure transducer described above to monitor the surface temperature of the sample and gas pressure in the vessel during carbonation curing. This system was integrated with operation software — Strain Smart Version 2.21. This application allowed data do be converted directly to engineering units, reduced and recorded at specified intervals.

3.2 Materials

3.2.1 Cementitious Binder

A CSA type 10 St Lawrence Portland cement was used as cementitious binder in this project. Its chemical analysis and mineralogical composition are as shown in Table 3.3 and 3.4, respectively. The fineness of the as received cement is 373m^2/kg and its specific gravity is 3.14.

Table 3. 3: Chemical composition of type 10 Portland cement (wt %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2Oe	LOI	CO_2
63.1	19.8	4.9	2.0	2.0	3.8	0.85	2.8	0.54

Table 3. 4: Mineralogical composition of type 10 Portland cement (wt %)

C_3S	C_2S	C_3A	C_4AF
59.3	12.1	9.5	6.2

3.2.2 Normal Weight Aggregate

Fine aggregate used in both concrete compacts and pre-cast concrete samples is river sand with a fineness modulus of 2.3 and a specific gravity of 2.6. Coarse aggregate was prepared by crushing limestone with the size about 12mm (1/2 in). The limestone was crushed by a cone crusher and then sieved to collect portions of two sizes 2.36mm(#8)-4.75mm(#4) and 4.75mm(#4)- 6.45mm(#2). The specific gravity of air-dried limestone is 2.6.

3.2.3 Lightweight Aggregate (LWA)

Lightweight aggregate used in concrete compacts and precast concrete samples were prepared by crushing lightweight aggregate certified by Froehling and Roberson Inc. The lightweight aggregate was reduced in size with a cone crusher and then sieved to collect the portion with the size between 2.36mm(#8) and 4.75 mm (#4).

Lightweight aggregate was immersed in de-ionized water in 24 hours and then surface dried in order to act as a water reservoir to compensate both water loss during carbonation reaction and water evaporation in the process of presetting and drying. Pre-soaked LWA with size of 2.36mm(#8)-4.75mm(#4) was used to partially or completely replace limestone of same size in concrete compacts or pre-cast concrete samples. Specific gravity and absorption capacity of pre-soaked LWA (surface dry condition) were determined based on water displacement method and ASTM C127-01 and AASHTO No.T85.

It is well known that lightweight aggregate (LWA) take a long time to reach saturation in water. This not only makes the determination of water absorption capacity difficult, but also hampers the use of saturated LWA as an internal curing agent. However, it is not practical to immerse LWA in water for such a long period of time to obtain potential absorption. As a matter of fact, storage of LWA in water for 24 hours before concrete mixing is an established practice in LWA production technology (Lura, 2005).

Before any mix design was made on concrete compacts, the specific gravity and absorption capacity of pre-soaked LWA were determined. Absorption is defined as the increase in weight of aggregate due to water uptake, but not including the moisture adhering to the outer surface of the particles. The specific gravity of pre-soaked LWA with surface dry is the ratio of the mass in air of a unit volume of aggregate to the weight in air of an equal volume of gas-free distilled water at a stated temperature. Water displacement method provides a rapid procedure to determine specific gravity of LWA with surface dry. Water absorption of pre-soaked LWA was determined based on ASTM C127-01 and AASHTO No.T85. Absorption capacity of LWA will determine the mass of pre-soaked LWA to replace partial limestone, if required moisture content is known. Specific gravity of LWA is the value desired for mixture design based on volume method.

The sample aggregate for absorption test was sieved to maintain a particle size in a range of 2.36mm(#8)-4.75mm(#4). LWA retained on the sieve was thoroughly washed to remove dust and other coatings from surface. 800g air-dried LWA was weighed and used as test sample. The apparatus of the test consists of the following device:

- A balance with an accuracy of 0.1g.
- A wire basket as the sample container with mesh size smaller than 2.36mm(#8).
- A watertight tank big enough to completely immerse the aggregate and the sample container, equipped with an overflow valve to keep the water level constant.
- A wire used to suspend the sample container with the smallest practical diameter in order to reduce any effects of a variable immersed length.

The following tests were performed and each weighing was made to the nearest 0.1g:

1. The test sample was dried to a constant weight in an over at a temperature of 110 ± 5°C and subsequently cooled in air at room temperature for 1 to 3 hours. After the cooling period, the sample was immersed in water at room temperature for 24 ± 4 hours.
2. After the test sample in the wire basket was removed from the water, an absorbent towel was used to roll the sample until there was no free water on the surface of

the sample. Subsequently, the weight of the sample with surface dry was recorded as M_1 (g) in air.

3. The empty wire basket was totally immersed into water and great care should be taken to avoid air trapped when the container was submerged. Adjust the water level just below the overflow spout of the tank until no water can flow out.
4. A 1000ml beaker was placed below the overflow spout to collect water overflowing from valve of the water tank. After determining the mass of sample in air, the test sample was removed to the dry basket and completely inundated in water. Take care to prevent any entrapped air by shaking the container while submerging. The water in the beaker was weighed and recorded as M_2 (g).
5. The test sample in a container was dried to a constant weight in an over regulated at 110 ± 5°C and then cooled in air at room temperature for 1 to 3 hours or until the sample could be comfortably handled. The oven-dry weight of the sample was recorded as M_3 (g).

Calculations were performed based on Archimedes's principle and formula in ASTM C127-01 for desired results. The specific gravity and water absorption of pre-soaked LWA with surface dry was summarized in Table 3.5.

$$\text{Specific Gravity (surface dry)} = M_1 / M_2 \quad (3.1)$$

$$\text{Absorption Capacity in 24 hours (\%)} = 100*(M_1 - M_3)/ M_3 \quad (3.2)$$

Where:

M_1 (g) = mass of 24-hour soaked LWA with surface dry in air

M_2 (g) = mass of water displaced by pre-soaked LWA with surface dry

M_3 (g) = mass of oven-dry LWA in air

Table 3. 5: Specific gravity and water absorption of 24-hour soaked LWA with surface dry

M_1 (g)	M_2 (g)	M_3 (g)	Specific Gravity	Water Absorption Capacity
897.6	566.9	791.1	1.6	13.5%

3.2.4 Chemical Admixture — Solvitose FC 100

Solvitose FC 100 provided by AVEBE is a starch-based additive facilitates production of concrete paving blocks and kerbstone. It is a shape stabilizer for moulded concrete block produced on vibrator and hydraulic press machines. Therefore, the capability for filling of moulds and dimensional stability of concrete block are improved tremendously. A higher water to cement ratio can be used without loss of workability, creating a stable mix and causing the cement to harden better. Consequently, better strength can be achieved using Solvitose FC 100 at the same water to cement ratio. This is verified by results from AVEBE that use of Solvitose FC 100 and more water lead to increased density and flexural tensile strength after 7 and 28 days. In this project, it is expected that the use of Solvitose FC 100 could reduce water evaporation during carbonation and maintain more water for better hydration and gain better flexural and compressive strength of carbonated concrete compacts and pre-cast concrete specimens up to 28 days. Dosage of 0.1% of cement content was used based on the recommendation from manufacturer. And a high ratio of 2% was also investigated to for any additional benefits.

3.3 Mixture Proportion and Sample Preparation

3.3.1 Cement Paste Compacts

The cement content for every cement paste sample was kept same as 240g and water to cement ratio was fixed at 0.15. Required proportion of cement and water were mixed according to the batch mix design shown in Table 3.6. Cement and de-ionized water were mixed for approximately 5 minutes to produce a paste using a kitchen mixer. After mixing, the paste was measured to keep each specimen the same weight in order to obtain same thickness after compaction. The mixture was poured into moulds with a 76mm width by 127mm length and was flatted to keep the top and bottom surface parallel. During moulding, a dampen board was covered over the mixing bowl in order to prevent water evaporation. Then, all the plate samples were press-formed by MTS machine to a peak load of 77kN, yielding a compaction pressure of 8MPa. The thickness of each

cement paste sample was approximately 14mm after compaction. After demoulding, the compacts were stored in a sealed chamber to minimize water loss until all the samples were completely made. The hydrated reference samples can't be placed under water immediately after compaction and should be placed in moisture chamber in the first 24 hours in order to achieve sufficient strength for curing in water. If the specimens were carbonated before hydration, they can be cured in water immediately after treatment with carbon dioxide. For the samples cured in water, they should be removed for air drying one day before the test date.

Table 3. 6: Batch mix design of cement paste compacts

Batch	No. of Samples	Cement (g)	De-ionized Water (g)	w/c	Weight per Sample (g)
P1C	2	480	72	0.15	276
P2CB	6	1440	216	0.15	276
P3CB	6	1440	216	0.15	276
P4CW	6	1440	216	0.15	276
P5CW	6	1440	216	0.15	276
P6C	6	1440	216	0.15	276
P7CW	6	1440	216	0.15	276
P8CW	6	1440	216	0.15	276
P9HW	4	960	144	0.15	276
P10HB	4	960	144	0.15	276

Note: P=cement paste compact, C=carbonation, H=hydration, B=subsequent hydration in sealed bags, W=subsequent hydration in water.

Carbonation and hydration condition for each batch are presented in Table 3.7.

- Batch P1C has only two samples carbonated simultaneously. Its carbonation characteristics were compared with batch where six samples were carbonated together to study batch size effect.
- Batch P2CB and P4CW were carbonated at gas pressure of 0.5 MPa while batch P3CB and P5CW were carbonated at gas pressure of 0.15MPa. The comparison would show the gas pressure effect.
- Strength development and pH evaluation of carbonated samples were monitored in different normal curing process, such as in water (W) and in sealed plastic bags (B), at the age of 4 and 28 days.

- Four-day continuous carbonation in a moist environment was conducted on batch P6C to investigate effect of prolonged treatment on fresh cement paste compacts.
- Effect of Carbon dioxide exposure time was studied using batch P7CW and P8CW with 1-hour and 30-minute carbonation respectively.
- Batch P9HW and P10HB are hydration references cured in water and sealed bags respectively.

3.3.2 Concrete Compacts

Mixture proportion of limestone concrete samples (without LWA) in batch C1HB, C3CB, C6CB and C7CB was determined with following parameters:

- To simulate concrete block in real production, the cement content in limestone concrete compact (without LWA) was 19%.
- Cement/sand/limestone =1:2:2 (by mass)
- Sand/limestone = 1:1 (by volume).
- Limestone (2.36mm-4.75mm) to limestone (4.75mm-6.35mm) ratio by volume is 1:1.
- Water/cement = 0.26

As each concrete compact has a dimension with 127mm in length by 76mm in width by 20mm in depth, mix proportion of limestone concrete samples with treatment of pre-soaked LWA was determined with considerations as follows:

- The same amount of cement and sand was used as that in limestone concrete compact (without LWA).
- Sand / (limestone + LWA) =1:1 (by volume).
- Effective water to cement ratio (mixing water content/cement content) = 0.20, 0.26.
- For mixture proportion of batch of limestone concrete treated with pre-soaked LWA, calculations were performed on mass of pre-soaked LWA and mass of limestone replaced by LWA, shown in Table 3.8.

Table 3. 7: Curing conditions of cement paste compacts

Batch	Carbonation-hydration or hydration	
P1C	P1C0	2 hour carbonation at 0.5 MPa
P2CB	P2CB0	2 hour carbonation at 0.5 MPa
	P2CB4	2 hour carbonation at 0.5 MPa + 4 day hydration in sealed bags
	P2CB28	2 hour carbonation at 0.5 MPa + 28 day hydration in sealed bags
P3CB	P3CB0	2 hour carbonation at 0.15 MPa
	P3CB4	2 hour carbonation at 0.15 MPa + 4 day hydration in sealed bags
	P3CB28	2 hour carbonation at 0.15 MPa + 28 day hydration in sealed bags
P4CW	P4CW0	2 hour carbonation at 0.5 MPa
	P4CW4	2 hour carbonation at 0.5 MPa + 3 day hydration in water + 1 day hydration in the air
	P4CW28	2 hour carbonation at 0.5 MPa + 27 day hydration in water + 1 day hydration in the air
P5CW	P5CW0	2 hour carbonation at 0.15 MPa
	P5CW4	2 hour carbonation at 0.15 MPa + 3 day hydration in water + 1 day hydration in the air
	P5CW28	2 hour carbonation at 0.15 MPa + 27 day hydration in water + 1 day hydration in the air
P6C	P6C4	4 day carbonation at 0.15 MPa, with water on the bottom of the vessel to obtain moisturized gas)
P7CW	P7CW0	1 hour carbonation at 0.15 MPa
	P7CW4	1 hour carbonation at 0.15 MPa + 3 day hydration in water + 1 day hydration in the air
	P7CW28	1 hour carbonation at 0.15 MPa + 27 day hydration in water + 1 day hydration in the air
P8CW	P8CW0	30 minute carbonation at 0.15 MPa
	P8CW4	30 minute carbonation at 0.15 MPa + 3 day hydration in water + 1 day hydration in the air
	P8CW28	30 minute carbonation at 0.15 MPa + 27 day hydration in water + 1 day hydration in the air
P9HW	P9HW4	1 day hydration in moist chamber+ 2 day hydration in water + 1 day hydration in the air
	P9HW28	1 day hydration in moist chamber+ 26 day hydration in water + 1 day hydration in the air
P10HB	P10HB4	4 day hydration in sealed bags
	P10HB28	28 day hydration in sealed bags

Note: P=cement paste compact, C=carbonation, H=hydration, B=subsequent hydration in sealed bags, W=subsequent hydration in water.

Table 3. 8: Weight of pre-soaked LWA and limestone in concrete compacts

Number of Samples	6
Water Carried In by LWA(g)	30.6[1]
Mass of Pre-soaked LWA (g)	30.6+30.6÷13.5%[2]=257.3
Volume of Pre-soaked LWA (cm^3)	257.3÷1.6[3]=160.8
Volume of Limestone Replaced by LWA (cm^3)	160.8
Mass of Limestone Replaced by LWA (g)	160.8 × 2.6[4]=418.1
Mass of Limestone (g)	493.8-418.1=75.7

Note: 1. water loss determined from 2-hour carbonation of limestone concrete without LWA
2. 24-hour absorption capacity of LWA =13.5%
3. Specific gravity of 24-hour soaked LWA (saturated surface dry) = 1.6
4. Specific gravity of limestone = 2.6

Table 3. 9: Batch mix design of concrete compacts

Composition	C1HB	C2HB	C*3C**B	C4CB	C5CB	C6CB	C7CB
No. of Samples	3	3	6	6	6	6	6
Cement(g)	246.9	246.9	493.8	493.8	493.8	493.8	493.8
River Sand(g)	493.8	493.8	987.6	987.6	987.6	987.6	987.6
Limestone 2.36~4.75mm (g)	246.9	37.9	493.8	75.7	75.7	493.8	493.8
Limestone 4.75~6.35mm (g)	246.9	246.9	493.8	493.8	493.8	493.8	493.8
Pre-soaked LWA 2.36-4.75mm (g)	0	128.6	0	257.3	257.3	0	0
Water Carried In by LWA (g)	0	15.3	0	30.6	30.6	0	0
Mixing DI water (g)	64.2	48.9	128.4	97.8	128.4	128.4	128.4
Solvitose FC100 (g)	0	0	0	0	0	0.494	9.876
Water/Binder	0.26	0.20[1] +0.06[2]	0.26	0.20[1] +0.06[2]	0.26[1] +0.06[2]	0.26	0.26
Total Mass (g)	1298.7	1203.0	2597.4	2406.0	2436.6	2597.9	2607.3

Note: 1 C*=concrete, C**=carbonation, H=hydration, B=subsequent hydration in sealed bags
2 It is defined as effective water to cement ratio, the ratio of mixing water content to cement content
3 It is the ratio of water content absorbed by LWA to cement content

Table 3.9 shows the batch mix design of concrete compacts and Table 3.10 summarizes carbonation and hydration condition for each batch. Limestone concrete compact is the basic batch. Its mixture proportion and forming process followed closely the industry production for masonry units and paving stones. C1HB is the reference limestone concrete hydrated for 28 days in sealed bags. Batch C3CB was limestone concrete

compact, treated by carbonation at 0.15 MPa for 2 hours, to quantify CO_2 uptake water loss and strength and to be compared with the batch C1HB.

Two approaches were investigated to compensate water loss and to improve mechanical performance of carbonated concrete compacts. In batch C4CB and C5CB, pre-soaked LWA was applied to act as a water reservoir with different effective water to cement ratio of 0.20 and 0.26 respectively. Effective water to cement ratio is defined as the ratio of mixing water content to cement content. The batch C2HB were prepared as hydrated reference of concrete compacts with LWA for comparison with the batch C4CB and C5CB. Different dosage of Solvitose FC 100 was used in batch C6CB and C7CB to prevent great water loss during carbonation and to improve strength of carbonated samples up to 28 days. In these batches, all samples were treated with carbon dioxide at gas pressure of 0.15 MPa for 2 hours. All carbonated and non-carbonated samples were cured in sealed bags for 28 days in order to investigate effectiveness of pre-soaked LWA as internal curing agent and Solvitose FC 100 as a water retainer.

3.3.3 Precast Concrete with Reinforcement

Based on the observation that early age carbonation does not significantly reduce pH value of cement paste compacts and concrete compacts below 11.5, a feasibility study was carried out on carbonation curing of precast concrete to explore wider applications of concrete production and their related technical benefits. Lightweight aggregate concrete and limestone concrete were prepared in batches PC1 and PC2 respectively. LWA with size 2.36mm(#8)-4.75mm(#4) was submerged in water for 24 hours and drained to surface dry for use in batch PC1. The specific density and absorption capacity of pre-soaked LWA were as same as described in Table 3.3. Air-dried limestone of particle size between 2.36mm(#8)-4.75mm(#4) was used in batch PC2.

Table 3. 10: Carbonation and hydration conditions of concrete compacts

Batch	Description	Carbonation-hydration or/and hydration samples	
C1HB	Hydrated reference concrete with limestone	C1HB28	28-day hydration in sealed bags
C2HB	Hydrated reference concrete using limestone and pre-soaked LWA	C2HB28	28-day hydration in sealed bags
C*3C**B	Carbonated reference concrete with limestone	C3CB0	2 hour carbonation at 0.15 MPa
		C3CB28	2 hour carbonation at 0.15 MPa + 28 day hydration in sealed bags
C4CB	Carbonated concrete using limestone and pre-soaked LWA	C4CB0	2 hour carbonation at 0.15 MPa
		C4CB28	2 hour carbonation at 0.15 MPa + 28 day hydration in sealed bags
C5CB	Carbonated concrete using limestone and pre-soaked LWA	C5CB0	2 hour carbonation at 0.15 MPa
		C5CB28	2 hour carbonation at 0.15 MPa+ 28 day hydration in sealed bags
C6CB	Carbonated concrete using limestone with Solvitose FC 100 (0.1% of cement by weight)	C6CB0	2 hour carbonation at 0.15 MPa
		C6CB28	2 hour carbonation at 0.15 MPa + 28 day hydration in sealed bags
C7CB	Carbonated concrete using limestone with Solvitose FC 100 (2% of cement by weight)	C7CB0	2 hour carbonation at 0.15 MPa
		C7CB28	2 hour carbonation at 0.15 MPa + 28 day hydration in sealed bags

Note: C*=concrete compact, C**=carbonation, H=hydration, B=subsequent hydration in sealed bags

Each precast concrete has a dimension with 127mm in length by 76mm in width by 30mm in depth. Mix proportioning of precast concrete samples was determined using volume-based method with following considerations:

- The volume of cement paste or cementitious binder should be in the range of 0.28-0.35m^3 for 1m^3 concrete.

- The amount of cement was the same as used in concrete compacts and expressed in kg/m^3.
- The consistency or workability of the concrete was the main concern. Prior to final proportioning, various water/cement ratios were attempted to make casting available. Finally water to cement ratio of 0.48 was selected.
- Total volume of aggregate was $0.66m^3$ for $1m^3$ concrete, the same as used in concrete compacts.
- Volume ratio of fine and coarse aggregate was set to be 2:3 for a better flow property.
- Calculations of weight of coarse and fine aggregate in batches PC1 and PC2 were summarized in Table 3.11.

Table 3. 11: Weight of coarse and fine aggregate in precast concrete batches

PC1		PC2	
LWA/ sand (by volume)	1.5	Limestone/Sand (by volume)	1.5
Total LWA and Sand (by volume)	0.66	Total Limestone and Sand (by volume)	0.66
LWA (m^3/ m^3)	0.393	Limestone (m^3/ m^3)	0.393
Sand (m^3/ m^3)	0.262	Sand (m^3/ m^3)	0.262
LWA(g/m^3)	629.411	Limestone (g/m^3)	1022.794
Sand (g/m^3)	681.862	Sand (g/m^3)	681.862

Note: Specific gravity of river sand (air dry) =2.6
Specific gravity of limestone (air day) =2.6
Specific gravity of pre-soaked LWA (surface dry) =1.6

Mix proportion is shown in Table 3.12. For each batch, 10% extra material was added in casting and eighteen samples were made simultaneously. Each concrete sample was cast in a dimension of 127mm by 76mm by 30mm mould with a medium vibration on a vibration table. Four different treatments were conducted in each batch as described in Table 3.13. In both two batches, process of presetting and/or drying is required prior to carbonation curing because much moisture on the sample surface will limit carbonation reaction although appropriate amount of water is actually needed for treatment with carbon dioxide. Where presetting, a kind of partial hydration process, was required the samples were simply left in air. Drying of preset samples was performed at $50^{\circ}C$ for 1

hour. Carbonation curing was conducted under a pressure of 0.15 MPa for 2 hours followed by subsequent hydration in moist room up to 28 days. For the samples cured in moist room, they should be removed for air drying one day before the test date.

Table 3. 12: Batch mix design of precast concrete

Composition	PC1		PC2	
	kg/m^3	Mass for mixing (g)	kg/m^3	Mass for mixing (g)
Cement	426.164	2443.3	426.164	2443.3
River Sand	681.862	3909.3	681.862	3909.3
Limestone 2.36~4.75mm	/	/	1022.794	5864.0
Pre-soaked LWA 2.36~4.75mm	629.411	3608.6	/	/
Total Water	204.559	1172.8	204.559	1172.8
Solvitose FC 100 (0.1%)	0.426	2.4	0.426	2.4
Water Carried In by LWA	84.971	487.2	/	/
Water/Binder	0.48^1 + 0.20^2	$0.48^1 + 0.20^2$	0.48	0.48
Total Mass	1942.423	11136.5	2335.805	13391.8
Cement Content (%)	0.219		0.182	
Water Content (%)	0.149		0.088	

Note: 1 It is defined as effective water to cement ratio, the ratio of mixing water content to cement content

2 It is the ratio of water content absorbed by LWA to cement content

Table 3. 13: Batches of precast concrete

Batch	carbonation and hydration		No. of samples
PC1	PC1H	21 hour preset	3
	PC1H28	21 hour preset + 26 day hydration in moisture room + 1 day in air	3
	PC1HC	18 hour preset +1 hour drying + 2 hour carbonation at 0.15 MPa	6
	PC1HC28	18 hour preset + 1 hour drying + 2 hour carbonation at 0.15 MPa + 26 day hydration in moisture room + 1 day in air	6
PC2	PC2H	21 hour preset	3
	PC2H28	21 hour preset + 26 day hydration in moisture room + 1 day in air	3
	PC2HC	19 hour preset + 2 hour carbonation at 0.15 MPa	6
	PC2HC28	18 hour preset + 2 hour carbonation at 0.15 MPa + 26 day hydration in moisture room + 1 day in air	6

Note: PC=precast concrete, C=carbonation, H=hydration, 28=at age of 28 days

3.4 Performance Assessment

The following experiments are described in detail for performance evaluation of all carbonated samples including cement paste compacts, concrete compacts and precast concrete with reinforcement.

3.4.1 Water Loss during Presetting and Drying

Only for the pre-cast concrete batch, a process of presetting and/or drying was performed before carbonation curing. Because preset samples were simply left in air instead of in sealed moist environment, water evaporation is significant during this process. Consequently monitoring water loss was performed during the entire process before carbonation curing. Two different balance systems were applied for mass recording: 1) the mass loss of samples was recorded every 10 minutes with in-situ Ohaus Digital Balance System; 2) samples before and after presetting were weighed using regular electronic scale. Drying in oven at 50°C is another method to remove some moisture from surface of samples. Mass change during 1 hour drying was recoded every 10 minutes with electric balance.

3.4.2 Characteristics of Carbonation Curing

For the batches under CO_2 treatment, the mass of each sample was measured using electronic balance with accuracy of 0.1g before carbonation curing. A thermocouple equipped in curing vessel was attached to the surface of one of these samples. After the vessel was sealed, 100% CO_2 was injected to reach certain pressure level. During carbonation curing, the readings of pressure gauge and the temperature variation were recorded by data acquisition system through a pressure transducer and a thermocouple, respectively. Immediately after completing CO_2 curing process, the gas was released and the mass of each sample was recorded and the total water loss during carbonation was collected using absorbent paper.

1) Temperature and Pressure Curves

The temperature and pressure of the sample during carbonation reaction was recorded by acquisition system with a thermocouple and a pressure transducer. Gas pressure during carbonation curing was kept constant either at 0.5 MPa and 0.15 MPa. The reaction of carbonation process is represented by temperature against time curve because it is a strong exothermal process that generates a large amount of heat. Peak temperature was recorded to evaluate the characteristic of carbonation reaction of cement paste, concrete compacts and pre-cast concrete samples under various treatment conditions.

2) Water Loss and Weight Gain (WG)

A measurement of CO_2 uptake per unit mass of dry cement during carbonation curing is defined as percentage of mass gain, which can be expressed by the following equation:

$$\text{Mass gain}\,(\%) = \frac{(\text{Mass})_{\text{aft,CO2}} - (\text{Mass})_{\text{bef,CO2}} + \text{Water}_{\text{lost}}}{(\text{Mass})_{\text{dry binder}}} \tag{3.3}$$

Where,

$(\text{Mass})_{\text{bef,CO2}}$ = the mass recorded before carbonation curing,

$(\text{Mass})_{\text{aft,CO2}}$ = the mass after carbonation curing.

A Water loss results from moisture evaporation, which is condensed on the wall of the curing vessel, because of the heat develops in carbonation reaction. On the one hand, total water loss during carbonation reaction should be recorded for correcting CO_2 uptake. On the other hand, the mass of water loss collected on the vessel wall and divided by total mixing water of each sample before carbonation represents the percentage water loss during carbonation curing. The mass of the dry binder is taken as the reference to define mass gain. The average mass gain was determined from all the samples carbonated in the curing vessel simultaneously. All readings were recorded by the balance with an accuracy of 0.1g.

3) Mass Curve (MC)

Mass curves can be obtained using in-situ Ohaus electronic balance system by recording mass change of the closed system with respect to exposure time in the entire carbonation process. Mass curves not only record the ultimate carbon dioxide uptake, but also effectively monitor the in-situ mass gain versus time. The efficient phase for carbon dioxide uptake can be identified during the whole carbonation curing. The typical mass curve of carbonation of cement paste compacts was shown in Figure 3.3. The CO_2 uptake obtained from mass curve should be corrected because there is weight difference between mass of residual gas after carbonation and mass of air before carbonation without vacuum. The correction procedure was followed by the previous work at McGill University (Wang, 2007). For carbonation curing, CO_2 concentrations of the 0.5 MPa (≈5 atm) and 0.15 MPa (≈1.5 atm) CO_2 gas mixed with 1 atm air were estimated to be 5/(5+1)=83.3% and 1.5/(1.5+1)=60%, respectively. The mass of residual CO_2 equal to the weight difference of CO_2 gas and air at 1 atm was calculated from mass of pure CO_2 gas and air in curing vessel at different pressure (see Table 3.2) and summarized as follows.

(1) Six cement paste compacts carbonated at 0.5 MPa:

$$[(42.8/5)-(28.2/5)]\times 83.3\% = 2.43g$$

(2) Six cement paste compacts carbonated at 0.15 MPa:

$$[(12.9/1.5)-(8.5/1.5)]\times 60\% = 1.76g$$

(3) Six concrete compacts carbonated at 0.15 MPa:

$$[(12.4/1.5)-(8.2/1.5)]\times 60\% = 1.70g$$

(4) Six precast concrete samples carbonated at 0.15 MPa:

$$[(11.7/1.5)-(7.7/1.5)]\times 60\% = 1.59g$$

The corrected CO_2 uptake should be obtained by deducting the mass of residual CO_2 mass from total CO_2 mass gain m determined by mass curve (see Figure 3.3) according to Equation 3.4.

$$CO_2(g) = m - \text{residual } CO_2 \text{ mass in curing vessel} \qquad (3.4)$$

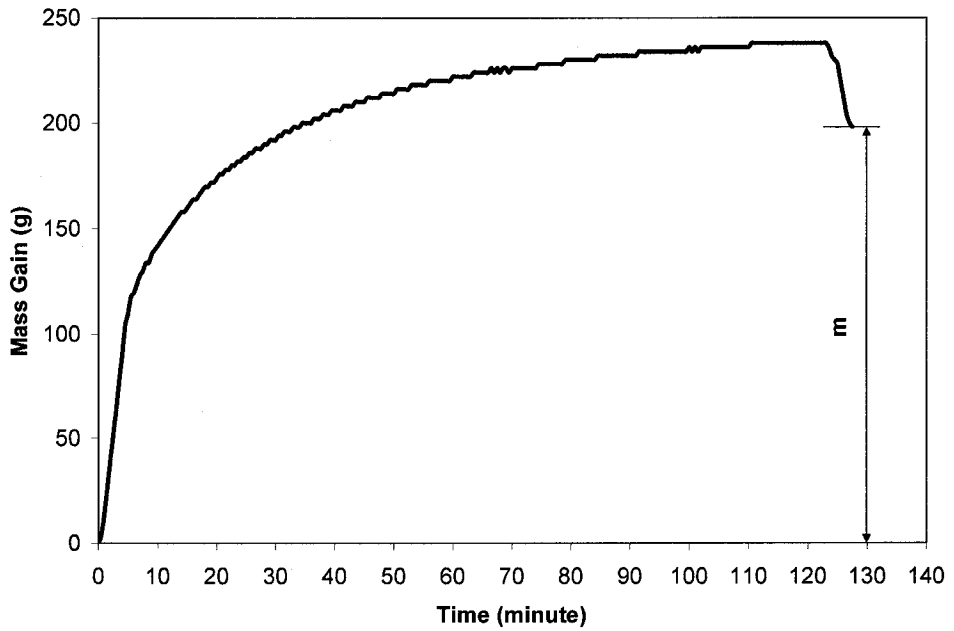


Figure 3. 3: Typical mass curve during carbonation of cement paste compacts

4) Constant-temperature Pyrolysis Techniques (PT)

Powder samples were also collected while preparing samples for pH assessment by suspension method. For cement paste compacts, pulverized samples were collected from the surface and the core separately using diamond drill. The crushed sample was finally sieved to pass 75μm mesh and collected for carbon dioxide content analysis.

The quantity of CO_2 uptake can also be determined through constant-temperature pyrolysis techniques. The carbonated sample was heated to three different temperature levels: 105°C, 500°C and 1000°C. The carbonated sample was dried at 105°C for 1 hour to remove free water, and then heated to 500°C for 1 hour. The weight difference between 105°C and 500°C was due to combined water. Eventually the sample was heated to 1000°C for 1 hour. The weight difference between 500°C and 1000°C was due to decomposition of carbonate and was equal to amount of CO_2 absorption. 1 g of each sample was heated and percentage of ignition at each temperature level was recorded respectively. The percentage of CO_2 uptake can be expressed in equation 3.5. The loss of

ignition at 1000°C was adjusted by 0.54%, which is the CO_2 content in as received cement.

$$CO_2 \text{ content}(\%) = \frac{\text{Mass}_{CO_2 \text{ evaporated at } 1000^\circ C}}{\text{Mass}_{\text{cement}}} = \frac{\text{Adjusted LOI at } 1000^\circ C \times 1(g)}{(1 - \text{total LOI}) \times 1(g)} \quad (3.5)$$

3.4.3 Three-point Bending Tests

Three-point bending tests were performed to determine the modulus of rupture (MOR) of cement paste and concrete compacts. Samples were examined as beams over a span of 101mm with an approximate width of 76mm and thickness of 14mm cement paste compacts and 20mm for concrete compacts respectively.

3.4.4 Compression Test

For cement paste and concrete compacts, three-point bending tests separated one sample of each batch into two half-pieces. Compression tests were then conducted on one half-piece of every sample with a compressive area of an average of surface and bottom load-bearing area. For precast concrete samples, compressive strength testing was performed on the whole sample with a cross section area of length by thickness.

3.4.5 Qualitative Depth of Carbonation

Carbonation of samples can be detected by using phenolphthalein indicator solution. A solution of 1% phenolphthalein and 70% ethyl alcohol is recommended to measure carbonation depth in hardened concrete by RILEM (1988). Phenolphthalein indicator solution was sprayed on the fresh broken surface immediately after three-point bending test. The colour pattern was observed and the pictures were taken immediately after indicator spraying. Phenolphthalein solution turns non-carbonated concrete red and remains colorless in carbonated concrete. It was known that such a solution can only indicate whether the PH-value is higher than 9.2 or not. Although, no depth of

carbonation was quantitatively measured, it was carried out to compare the colour patterns of carbonated samples with various treatments.

3.4.6 pH Measurement of Pore Solution

Suspension method was used for pH evaluation of carbonated cement-based products. This method is based on mixing pulverized powder sample with solvent and measuring the pH of the suspension by electrode. The validity of this method has been verified by comparing values to those calculated from titration results and measured from extracted solution with the use of high-pressure devices. The parameters affecting the pH assessment were investigated in detail (Räsänen and Penttala 2004) and were kept constant in this project as follows:

- The solvent used in all pH measurements was de-ionized water at room temperature.
- The powder-to-suspension ratio in the suspension method was 0.3.
- After drilling or crushing, the powder samples were sieved passing 75μm particle size fraction.
- The suspensions were mixed for 15 minutes with a magnetic stir bar.
- The suspension solutions were settled for 30 minutes after mixing.
- No filtration was required for suspensions since filtration has little effect on pH measurement.

For cement paste compacts, bulk powdered samples were prepared from control hydrated batches. Surface (≈ 2mm) and core of samples were collected from carbonated samples by using diamond drill separately. For concrete compacts, bulk crushed samples were obtained because there is a difficulty in separating the surface and the core of the concrete specimen with a depth of 20mm. For precast concrete samples, both surface and core specimens were collected by separating the surface layer of 5mm thick from the core using diamond saw.

12.86g of powder specimen and 30g de-ionized water were weighed both with an accuracy of 0.01g. They were immediately mixed together by using magnetic stir bars for

15 minutes. Then the pulverized sample was allowed to stand in de-ionized water for 30 minutes before 10ml of suspension was transferred into a small vial using a pipette without filtration. Finally, the pH measurement of suspension solution was performed using HANNA pH meter (range=-2.00~16.00 pH, accuracy=0.01pH) at a room temperature ($23^{\circ}C \pm 2^{\circ}C$) with a combination of electrode and Automatic Temperature Compensation (ATC) probe. The pH meter was calibrated by using two buffer solutions with pH values of 7.01 and 10.01 before each daily use. The pH value should be recorded when the change rate is less than 0.01 pH per minute. To verify the sensitivity of the pH measurement system, limestone powder, mainly composed of calcium carbonate, was tested as a reference prior to any pH measurement on cement-based products. The pH value of suspension solution of limestone powder was found to be 8.5, which was verified by other observations (Parrott and Killoh 1988).

3.4.7 X-ray Diffraction (XRD)

X-ray diffraction (XRD) analysis was performed using a Philips PW1710 Powder Diffractometer with Cu Kα radiation. Scanning was conducted at a 2θ from start position of 10° to end position of 60° and a 0.01° step size with 0.2 second per step. Powder samples were collected simultaneously with those prepared for carbon dioxide content analysis and pH measurement, as described in section 3.4.2.4.

Chapter 4 Results and Discussion

This Chapter presents the results and discussion on carbonation behaviour of cement paste compacts, concrete compacts and precast concrete, mainly to investigate the effect of early age carbonation on performances of concrete. For all batches of cement paste and concrete compacts treated with CO_2, peak temperature, water loss, mass curve and CO_2 mass gain were recorded. Mechanical tests, qualitative depth of carbonation and pH measurement of pore solution were conducted immediately after carbonation as well as after subsequent hydration. Carbon dioxide content analysis and X-ray diffraction were performed in batches of cement paste. In this project, a preliminary feasibility study was also conducted on carbonation curing of precast concrete. Two batches were investigated to study the effect of drying on characteristics of carbonation curing and performances of concrete after carbonation and subsequent hydration. Summaries of results were presented in this chapter and detailed experimental data were attached in Appendix A, B and C for cement paste compacts, concrete compacts and pre-cast concrete samples, respectively.

4.1 Performance of Carbonated Cement Paste Compacts

Various treatments of carbonation curing and hydration were applied for cement paste compacts to investigate their effects on carbonation behavior and performances of concrete up to 28 days. For treatment with carbon dioxide, there were two parameters involved: 1) levels of gas pressure at 0.5 MPa and 0.15 MPa, 2) carbonation curing durations of 2 hours, 1 hour, 30 minutes and 4 days. Furthermore, in subsequent hydration following carbonation, two hydration curing conditions in water and in sealed bags, were studied. Performance assessment of cement paste compacts was conducted immediately upon completion of carbonation and subsequently after 4 day and 28 day hydration.

4.1.1 Carbonation Curing Behavior

4.1.1.1 Effect of Batch Size

The batch size effect on carbonation behaviour was studied. Table 4.1 summarizes the characteristics of 2-hour carbonation for the batch P1C which contained only two samples and P2CB which had six samples carbonated together in the same vessel. The typical temperature and pressure curves during the carbonation curing of these two batches are displayed in Figure 4.1. The sample temperatures increased rapidly as soon as the carbon dioxide gas was injected into the pressure vessel. The temperature reached a peak within 30 minutes and gradually declined thereafter. When six samples were simultaneously carbonated, the maximum temperature was 38°C higher than that when only two samples were in the chamber. The more the concurrent exothermic reaction resources, the greater the heat liberated and the higher the peak temperature that was accelerated. Consequently, the influence of batch size on peak temperature was apparent. It was observed that more water loss as high as 16% occurred in batch P2CB of six samples. This might be attributed to greater heat evolution during reaction to expel more free water.

Although there was some difference in water loss, similar weight gain (WG) was obtained in these two batches (see Table 4.1). Therefore, it was conclusive that batch size significantly influenced peak temperature and water loss, while it had a negligible effect on carbon dioxide uptake. It is verified by CO_2 mass gain from mass curve (MC) readings and average CO_2 content of the surface and the core determined by constant-temperature pyrolysis techniques (PT) (see Table 4.1). For batch P1C with 2 samples simultaneously carbonated, amount of CO_2 absorbed by surface and core was in the same order of 11%; while for batch P2CB with 6 samples, CO_2 uptake in the core was 2.2% higher. It appeared that larger amount of water expelled by exothermic carbonation reaction led to more porous network in the core which facilitated CO_2 diffusion and thus yielded more uptakes.

To avoid batch size effect, six samples were thus prepared for each batch in the following studies with first two for immediate carbonation and others for subsequent hydration at age of 4 and 28 days.

Table 4. 1: Two-hour carbonation behavior (at gas pressure of 0.5 MPa) for cement paste compacts with different batch size

Batch	Peak Temperature (°C)	Water Loss[1] (%)	WG[2] (%)	MC[3] (%)	PT[4] (%)		
					Surface	Core	Average
P1C (2 samples)	81	30.5	12.2	13.5	11.9	11.8	11.9
P2CB (6 samples)	119	47.0	12.8	13.8	11.9	14.1	13.0

Note:

1 Ratio of water evaporated to total mixing water
2 Percentage of weight gain calculated from Equation 3.3
3 Percentage of CO_2 mass gains from mass curve readings
4 CO_2 uptake determined by constant-temperature pyrolysis techniques (Equation 3.5)

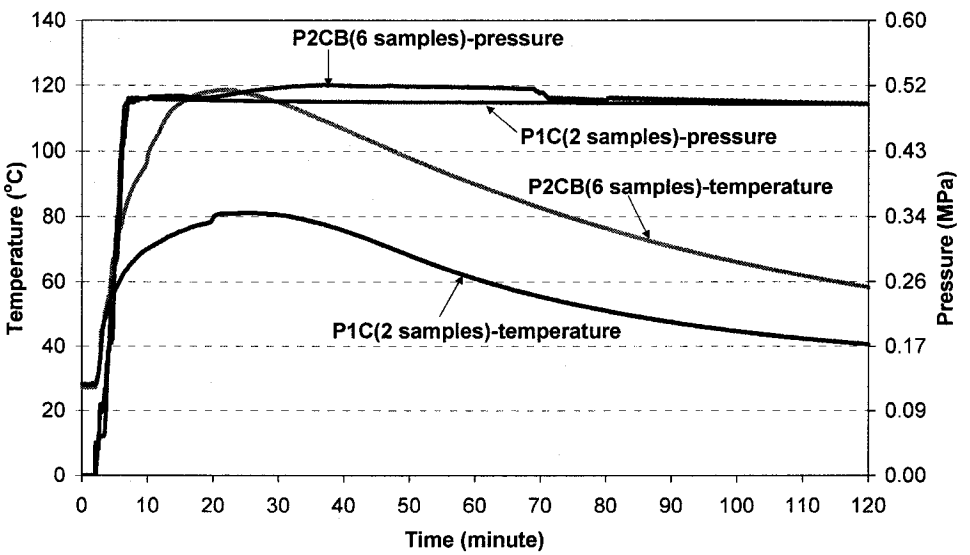


Figure 4. 1: Batch size effect on temperature and pressure curves during carbonation of cement paste compacts

4.1.1.2 Effect of Gas Pressure

The gas pressure effect on carbonation behaviour of cement paste compacts is summarized in Table 4.2. The typical temperature curves in carbonation curing for batches P2CB(0.5 MPa) and P3CB(0.15 MPa) are shown in Figure 4.2. The peak temperature was found to be slightly higher for carbonation at a gas pressure of 0.5MPa than at 0.15 MPa. At gas pressure of 0.15 MPa, a slower temperature decline was observed beyond reaching the maximum value. This might result in slightly larger amount of water loss because higher temperature was kept in the later stage of 2 hour carbonation. The difference in maximum temperature of different batches at the same pressure was attributed to the experimental variation. It was noticed that the content of CO_2 uptakes by weight gain (WG) method were on the same order, which can be well verified by CO_2 mass gain from mass curve (MC) readings and average CO_2 content of the surface and the core determined by constant-temperature pyrolysis techniques (PT) (see Table 4.2).

It was worth noting that CO_2 absorption determined by mass curve (MC) constantly exceeded that determined by weight gain (WG) method (see Table 4.1 and table 4.2). This might have occurred because the water vapour loss was unable to be collected while opening the vessel lid. From results determined by constant-temperature pyrolysis techniques (PT), it appeared that the core was more carbonated after 2 hour treatment because the core constantly had larger quantity of CO_2 uptake than that on the surface shown in Table 4.2. This might be due to more porous structure produced in the core as a result of significant water evaporation.

The typical mass curves shown in Figure 4.3 revealed a similar reaction rate at carbonation gas pressures of 0.5 MPa and 0.15 MPa. Two mass curves similarly displayed an increasing trend of CO_2 uptake within 60 minutes and a plateau afterward. The ultimate percent CO_2 content didn't increase greatly at higher gas pressure of 0.5 MPa. It was reported that increasing CO_2 pressure from 0.1 MPa to 0.2 MPa did increase the carbonation degree, but a further increase to 0.4 MPa had little additional effect

(Young *et al* 1974). It is, therefore, conclusive that high gas pressure carbonation is not energy efficient.

Table 4. 2: Two-hour carbonation behaviour for cement paste compacts at different gas pressures

Batch	Gas Pressure (MPa)	Peak Temperature (^{O}C)	Water Loss[1] (%)	WG[2] (%)	MC[3] (%)	PT[4] (%)		
						Surface	Core	Average
P2CB	0.5	119	47.0	12.8	13.8	11.9	14.1	13.0
P3CB	0.15	107	55.5	12.8	13.5	11.9	15.9	13.9
P4CW	0.5	118	50.6	13.6	14.5	13.0	15.7	14.4
P5CW	0.15	112	54.1	12.7	13.8	12.8	13.7	13.3

Note:

1 Ratio of water evaporated to total mixing water
2 Percentage of weight gain calculated from Equation 3.3
3 Percentage of CO_2 mass gains from mass curve readings
4 CO_2 uptake determined by constant-temperature pyrolysis techniques (Equation 3.5)

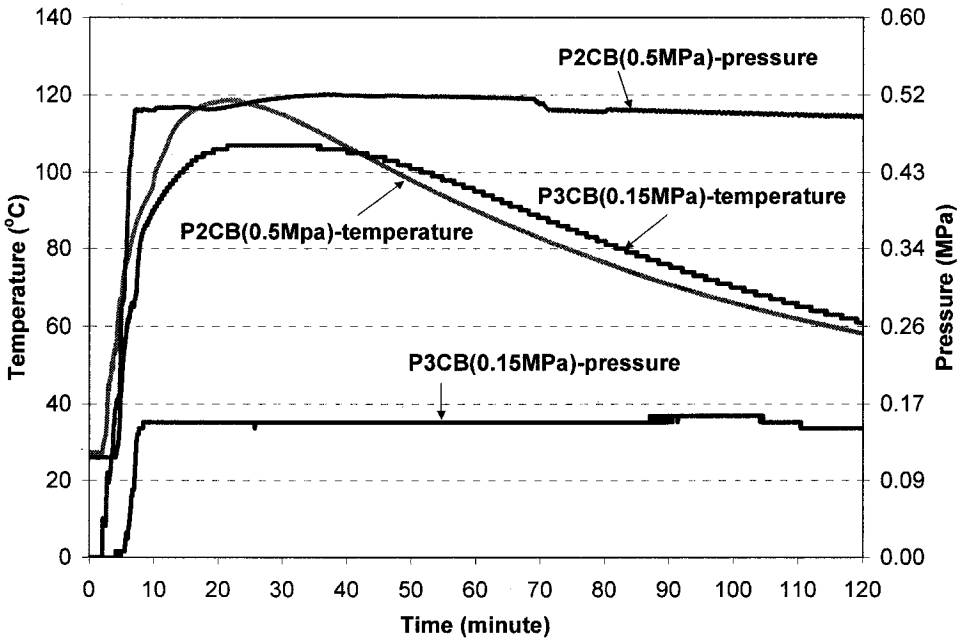


Figure 4. 2: Gas pressure effect on temperature curve during carbonation of cement paste compacts

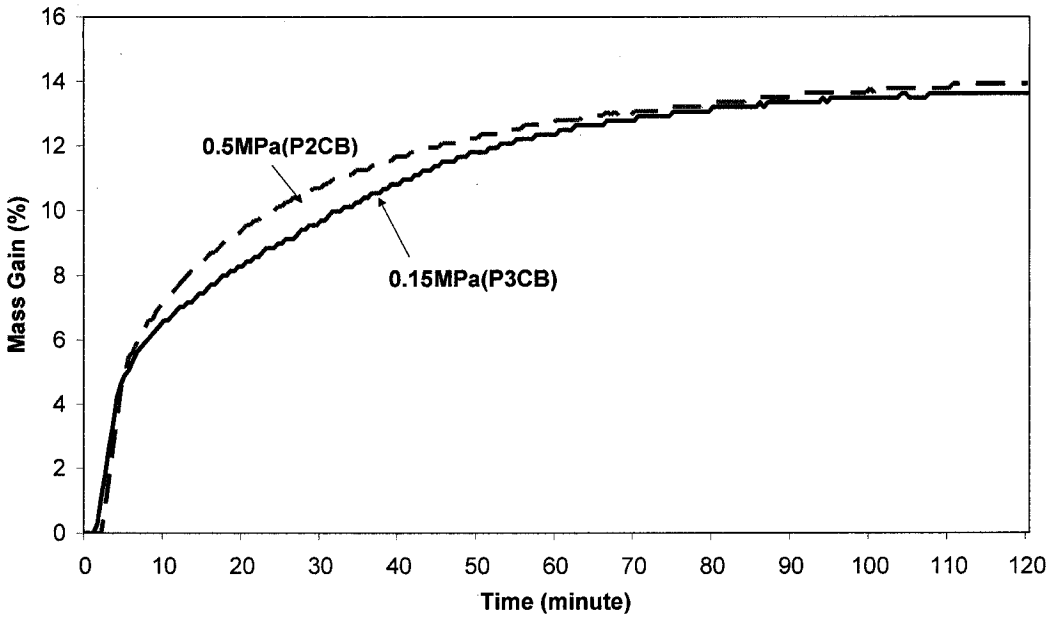


Figure 4. 3: Mass curves of cement paste compacts carbonated at different gas pressure

4.1.1.3 Effect of Exposure Time

Carbonation curing results for cement paste compacts exposed to various period of time are shown in Table 4.3. The duration of carbonation investigated was 2 hours, 1 hour, 30 minutes and 4 days to determine the effect of exposure time on carbonation behavior. Although the maximum temperature seemed to be higher for 2 hours than other exposure time, the discrepancies were primarily attributed to the experimental variation. Carbonation for 2 hours crated 8.36% and 19.37% more evaporated water than those for 1 hour and 30 minutes respectively. Based on results in Table 4.3, it could be seen that the majority of water was expelled at peak temperature due to rapid reaction in the initial period of carbonation process. Thereafter, carbonation reaction was slowed down gradually and produced less heat and evaporated less moisture in later period of the reaction. It was found that carbonation for a period of 2 hours resulted in 1.56% and 5.57% higher CO_2 uptake than those for 1 hour and 30 minutes. The relationship linking the percent CO_2 uptake to percentage water loss is shown in Figure 4.4. It indicated that for each mole water loss, there is 0.65 mole carbon gain for those carbonated samples. Larger amount of heat generated and consequently more water expelled by exothermic

carbonation reaction resulted in more pores in the sample, which facilitated more CO_2 ingress and thus yielded more uptakes. It is, therefore, inferred that carbonation degree, which is obtained based on CO_2 uptake, could be related to the water loss control during carbonation treatment.

Table 4. 3: Carbonation behaviour (at gas pressure of 0.15 MPa) for cement paste compacts with various exposure time

Batch	Carbonation Time	Peak Temperature (^{O}C)	Water Loss[1] (%)	WG[2] (%)	MC[3] (%)	PT[4] (%)		
						Surface	Core	Average
P3CB and P5CW	2 hour	110	54.8	12.8	13.7	12.4	14.8	13.6
P6C	96 hour,	103	/	/	14.7	14.0	16.0	15.0
P7CW	1 hour	101	46.5	11.2	12.1	11.5	10.4	11.0
P8CW	0.5 hour	100	35.4	7.2	8.7	11.5	8.0	9.8

Note:

1 Ratio of water evaporated to total mixing water
2 Percentage of weight gain calculated from Equation 3.3
3 Percentage of CO_2 mass gains from mass curve readings
4 CO_2 uptake determined by (constant-temperature pyrolysis techniques) Equation 3.5

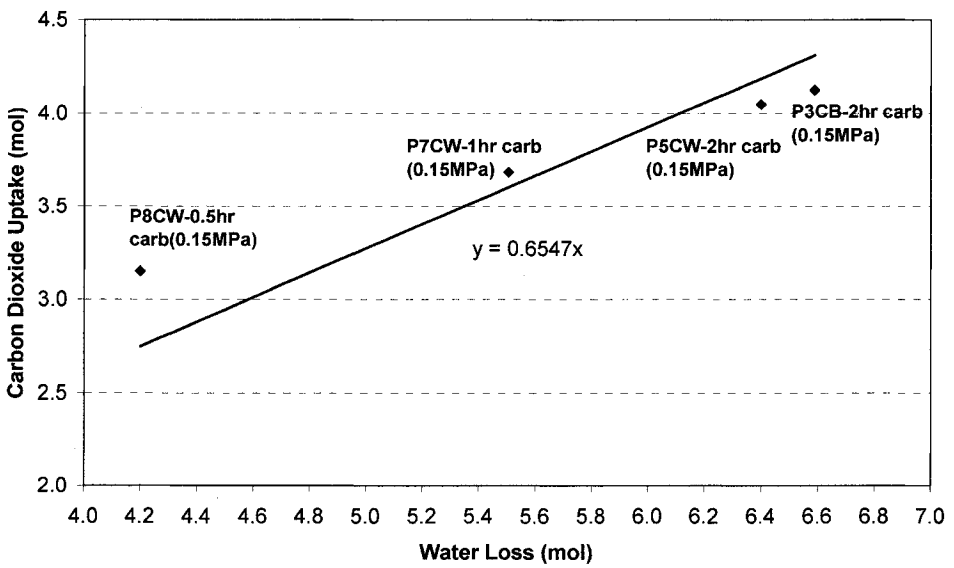


Figure 4. 4: Relationship between water loss and CO_2 uptake in carbonation for cement paste compacts

Water is an essential part of carbonation reaction and water starvation has been proposed to be the limiting factor to CO_2 uptake in carbonation reaction (Young *et al* 1974). It was proposed that water loss during carbonation may impede the potential reaction to approximately 25% of the maximum (Berger *et al* 1972). Water evaporation during carbonation treatment might hinder progressive reaction. To examine the mechanism of CO_2 capture limit, batch P6C was design to investigate the prolonged carbonation in the presence of moisture supply. Six samples were continuously carbonated for 4 days in the pressure vessel filled with water at the bottom so that the gas bubbled through the water and was moisturized before reacting with cement paste compacts. Because water loss and CO_2 uptake simultaneously exist during this system, only ultimate mass gain was recorded after 4-day continuous carbonation. The results are also presented in Table 4.3. It was found that carbonation for a period of 4 days resulted in 14.80% mass gain, 0.86% higher than that for 2 hours. It was indicated that even if samples were cured in the presence of moisture supply in a sufficient long period. It might be still difficult to sequester a large amount of CO_2. This could potentially be the result of build-up products formed on the surface of cement paste grain and retarded further the diffusion of CO_2 (Young *et al* 1974). It seems that it is not possible to achieve full carbonation on fresh samples through prolonged carbonation treatment.

From Table 4.3, it can be found that CO_2 uptake of the surface layer was in the same order of 11.5% for 30 minute and 1 hour carbonation. In other word, CO_2 absorption was little increased after 30 minutes. It was also observed that carbonation within 1 hour led to more CO_2 uptake in the surface than that in the core. On the contrary, it appeared that the core was more carbonated than the surface after 2 hour and 4 day carbonation treatment. This might be attributed to more porous structure produced in the core as a result of further water evaporation.

4.1.2 Mechanical Performance

Results for flexural and compressive strength testing of cement paste compacts are presented in this section. Both flexural and compressive strengths reported are average of two samples and the standard deviation is also noted. Effect of gas pressure effect, subsequent hydration conditions and effect of exposure time on mechanical properties of carbonated cement paste compacts are discussed by measuring immediate carbonation strength and later age strength.

4.1.2.1 Flexural Strength

Figure 4.5 shows flexural strengths obtained immediately after 2 hour carbonation as well as after 4 day and 28 day subsequent hydration. Comparison of the flexural strengths of samples immediately carbonated at different gas pressures (0.5 MPa and 0.15 MPa) indicated that 0.15 MPa led to a slightly higher strength gain. Thereafter, carbonated samples were either stored in water or cured in sealed bags for subsequent hydration. For samples cured in water, they were removed from water tank and dried in the air one day prior to strength testing. It was found that flexural strength of carbonated cement paste at gas pressure of 0.5 MPa could maintain the strength up to 28 days regardless of the subsequent hydration carried out in water or in sealed bags. For carbonated samples at gas pressure of 0.15 MPa, a reduction of 14.3% and 20.5% were found after 4 and 28 days respectively. It seemed that development of flexural strength was more related to gas pressure of carbonation than curing conditions in subsequent hydration. No beneficial influence was observed on flexural strength improvement of carbonated cement paste compacts even cured in water up to 28 days, although carbonation-generated flexural strengths were more than twice as high as those of conventionally hydrated samples after 4 and 28 days.

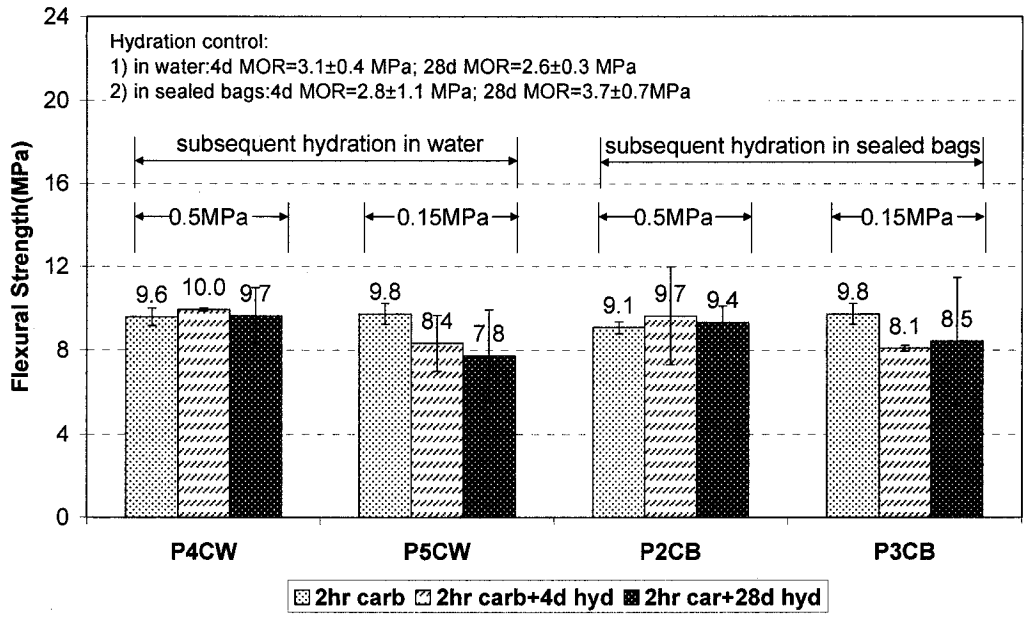


Figure 4. 5: Flexural strength of cement paste compacts after 2 hour carbonation and subsequent 28 day hydration

Effect of exposure time on flexural strength is shown in Figure 4.6 by comparing mass gain with strengths of carbonated samples in three batches, where gas pressure was kept at 0.15 MPa and carbonated samples were stored in water for subsequent hydration. The highest flexural strength of 9.75 MPa was achieved for samples immediately after 2 hour CO_2 treatment, 8% and 26% higher than those by 1 hour and 30 minute treatment respectively. The results indicated that flexural strength gain immediately after carbonation was dependent on carbon dioxide uptake within certain exposure time. In subsequent hydration process, flexural strengths were decreased by 21%, 14% and 34% in 2-hour carbonation (P5CW), 1-hour carbonation (P7CW) and 30-minute carbonation (P8CW), respectively; however, they were still much higher than that of their hydration reference. It was also observed that samples carbonated for 2 hours and 1 hour had similar flexural strength up to 28 days. It is inferred that although early-age flexural strength can be improved by carbonation curing, it might be unable to develop further strength in subsequent hydration at later age.

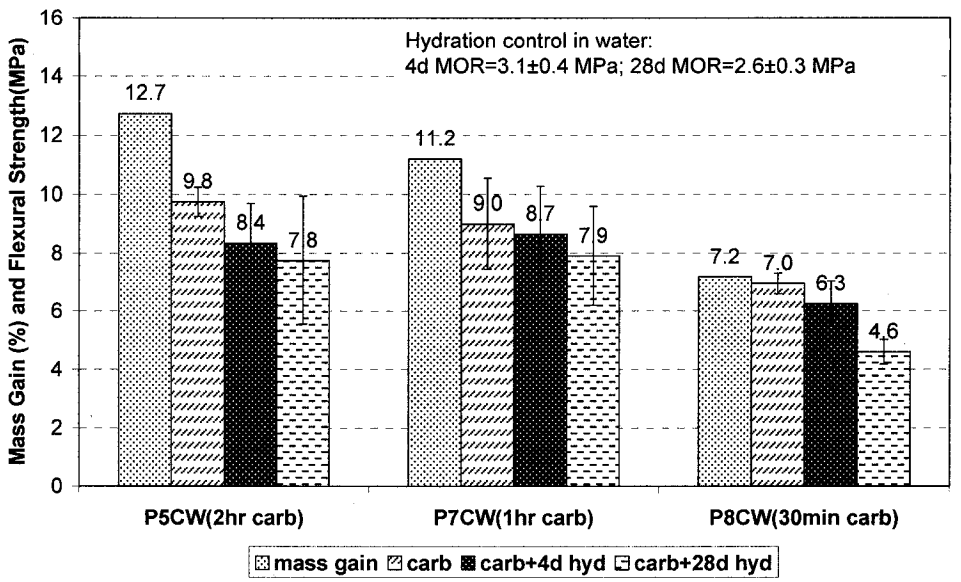


Figure 4. 6: Comparison between mass gain and flexural strength of cement paste compacts after carbonation up to subsequent 28 day hydration in water

Flexural strengths of compacts with different treatments after 4 days are shown in Table 4.4. Samples of different batches were examined at same age of 4 days but with various treatments prior to bending test. Samples of batch PC6 continuously exposed in CO_2 for 96 hours possessed over 20% higher flexural strength than those of samples through 2 hour carbonation and 4 day hydration. Thus, prolonged carbonation could have some contribution to flexural strength gain, which might have occurred due to a slightly more CO_2 uptake (see Table 4.3).

Table 4. 4: Flexural strength results of cement paste compacts with different treatments after 4 days

Batch	Carbonation Treatment and Hydration	Flexural Strength (MPa)
P6C	96 hour carbonation at 0.15 MPa with extra moisture	10.5±1.1
P3CB4	2 hour carbonation at 0.15 MPa + 4 day hydration in sealed bags	8.1±0.1
P5CW4	2 hour carbonation at 0.15 MPa+ 3 day hydration in water+ 1 day hydration in the air	8.4±1.3

4.1.2.2 Compressive Strength

Results of compressive strength immediately after 2 hour carbonation as well as after 4 day and 28 day hydration are shown in Figure 4.7. There was no noticeable difference of immediately carbonation generated compressive strengths at gas pressure of 0.5 MPa and 0.15 MPa possibly because their CO_2 uptakes were also very close. It is noted that development of compressive strength differed from that of flexural strength in the carbonation-hydration process. In subsequent hydration process, compressive strength of carbonated samples cured in water was found to have a slight increase at the age of 4 days, and a small decrease at 28 days. For carbonated samples cured in sealed bags, the variance in strength was in the range of standard deviation and was not considered as significant. Whether cured in water or cured in sealed bags, carbonated samples possessed a 28-day compressive strength, which was very close to 2-hour carbonation-generated strength. It seemed that hydration after carbonation wouldn't significantly improve the strength of samples. In these four batches, development of compressive strength was not influenced by gas pressure or curing conditions in subsequent hydration.

Compressive strengths of carbonated samples were assessed by comparing with those of hydrated samples cured in normal conditions at the same age. Reference samples hydrated in water possessed compressive strengths of 46.2 MPa at 4 days and 83.8 MPa at 28 days. The former was lower than that of carbonated samples but the latter was 43% higher. Compressive strength of hydrated compacts cured in sealed bags was 42.0MPa at 4 days and 38.8 MPa at 28 days. For subsequent hydration in sealed bags, carbonated cement paste compacts were stronger than their hydration reference. It is obvious that early age carbonation could reduce the hydraulic behaviour of cement in subsequent hydration even in the presence of moisture.

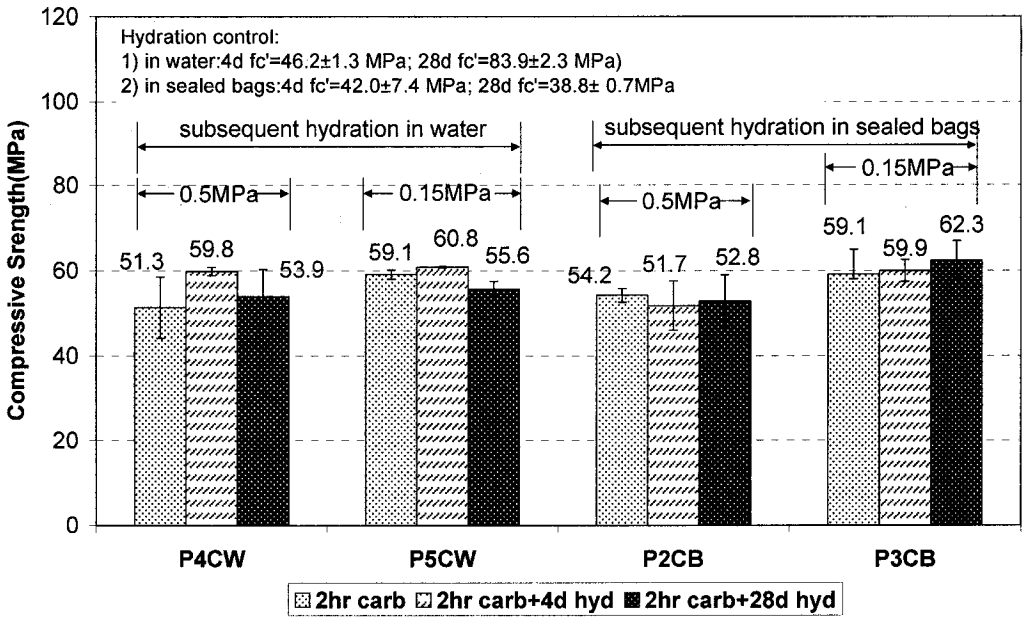


Figure 4. 7: Compressive strength of cement paste compacts after 2 hour carbonation and subsequent 28 day hydration

Effect of exposure time on compressive strength of carbonated samples is presented in Figure 4.8. Three batches were compared while keeping the constant gas pressure at 0.15 MPa and the subsequent hydration condition in water. Immediately 2-hour carbonated samples possessed the maximum compressive strength 59.1 MPa, 5.92% and 38.67% than carbonation by 1 hour and 30 minute respectively. It is indicated that, similar to flexural strength, compressive strength immediately after carbonation was also dependent on carbon dioxide uptake within certain exposure time. Although samples of 2 hour carbonation had highest early-age compressive strength up to 4 days, their 28 day strengths fell behind those with less carbonation. The strength of samples treated for 1 hour was well developed with 34% increase and became the highest of the three after 28 day hydration. Samples carbonated for 30 minutes had the most strength development with 78% increment and possessed the second highest strength up to 28 days. Therefore, the exposure for 1 hour seemed to be optimized by achieving both maximum flexural and compressive strength as well as second largest amount of carbon uptake. However, 28 day strengths of all carbonated batches were still lower than that of their hydration reference, which possessed the strength of 83.9 MPa. It is indicative that compressive

strength development of carbonated cement paste compacts can be monitored and optimized by varying exposure time of carbonation.

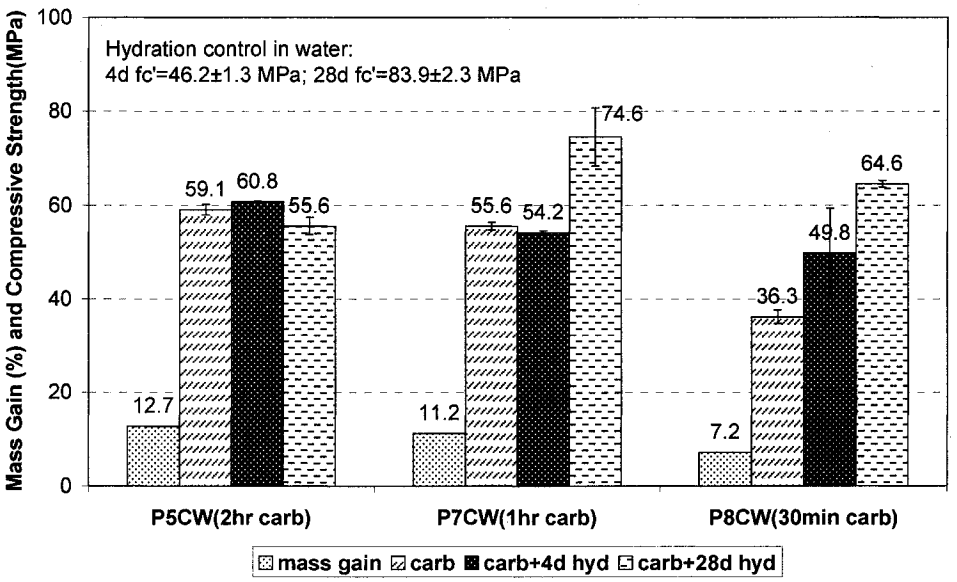


Figure 4. 8: Comparison between mass gain and compressive strength of cement paste compacts after carbonation and up to subsequent 28 day hydration in water

Table 4. 5: Compressive strength of cement paste compacts with different treatments after 4 days

Batch	Carbonation Treatment and Hydration	Compressive Strength(MPa)
P6C	96 hour carbonation at 0.15 MPa with extra moisture	58.3±0.5
P3CB4	2 hour carbonation at 0.15 MPa + 4 day hydration in sealed bags	59.9±2.6
P5CW4	2 hour carbonation 0.15 MPa + 3 day hydration in water+ 1 day hydration in the air	60.8±0.1

Compressive strengths of compacts with different treatments after 4 days are shown in Table 4.5. Samples of the batch P6C continuously carbonated for 96 hours had similar strength to those of samples through 2 hour carbonation and 4 day hydration. Almost no improvement of compressive strength was observed in prolonged exposure. It suggests

that compressive strength development cannot benefit from continuous prolonged carbonation and hydration happened simultaneously along with carbonation.

4.1.2.3 Discussion on 28-day Compressive Strength and CO_2 Uptake

It was found that 28-day compressive strength of carbonated cement paste compacts exceeded that of hydrated reference cured in sealed bags but did not catch up with that of hydration control through water curing. Similar phenomenon was reported by Klemm and Berger (1972) and Hannawayya (1984). Klemm and Berger conducted a research on whether subsequent hydration would significantly improve compressive strength. Type II mortars were formed under a compaction pressure of 5.9 MPa and carbonated at a gas pressure of 0.4 MPa for 5 minutes. It was reported that compressive strength of carbonated mortar samples plateaued about 31.0 MPa after 3 days and 14-day strength was 10.7% lower than that of conventionally hydrated samples cured in water. Strength development of carbonated mortar compacts was also investigated by Hannawayya. The mortar samples with a compaction pressure of 2.9 MPa were vacuum carbonated for 38 minutes. It was observed that 28-day compressive strengths of carbonated mortar compacts were about 31% lower than those of their hydration references regardless of curing in air or in water. It is therefore conclusive that there might be some influencing factors for long-term compressive strength of carbonated samples.

1) Water Loss during Carbonation Curing

It has been found that initial strength will be considerable and rapid through early-age carbonation, compared to that occurs with normal hydration (Young *et al* 1974). To summarize results in sections 4.1.2.1 and 4.1.2.2, hydration after carbonation wouldn't significantly improve both flexural and compressive strengths of samples and 22% decrease of flexural strength was found in carbonated samples by 2 hour carbonation. Although flexural strengths of carbonated samples always exceeded that of their hydrated references up to 28 days. It was also found that whether cured in water or cured in sealed bags, carbonated samples possessed similar compressive strength at 28 days. It was observed from Table 4.2 that initial water to cement ratio 0.15 was reduced to 0.07 after 2 hour carbonation. Thus, water remained inside was insufficient for further hydration

when samples were cured in sealed bags with no extra moisture provided. For reference samples cured in sealed bags for normal hydration, the strength was also not well developed because of the low water cement ratio of 0.15 and didn't catch up with that of carbonated samples cured in similar condition up to 28 days. This could be explained by the fact that water is a limiting factor for conventional hydration when low water to cement ratio is used for dry compact forming. Even if water curing was available for better hydration, the strength of carbonated cement paste compacts was not significantly improved yet. This might have occurred due to the following two reasons: (1) water absorption of specimens decreases considerably after carbonation curing (Hannawayya 1984), and thus less water will penetrate through the densified surface layer; (2) even if some extra moisture can be taken, it might not diffuse and react well with a large amount of non-hydrated materials which were coated by build-up carbonation products (Young *et al* 1974).

Calculated from percentage water loss in Table 4.3, carbonation time varying from 2 hours, 1 hour to 30 minutes resulted in ultimate water to cement ratios of 0.07, 0.08 and 0.10 respectively. No compressive strength improvement was found in 2-hour carbonated samples in the following hydration in water. 1-hour and 30-minute carbonated samples saw 34.08% and 78.21% increase in compressive strength after 28 days, respectively. Greater strength improvement might be due to higher ultimate water to cement ratio after carbonation and more water absorption resulted from less carbonation degree. It is thus conclusive that water loss during carbonation curing might be considered as one of limiting factors for strength development in subsequent hydration.

2) Carbon Dioxide Uptake

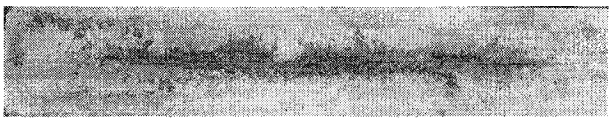
It seemed that gas pressure had somewhat effect on development of flexural strength up to 28 days, but had negligible influence on compressive strength. Compressive strength immediately after carbonation was dependent on the quantity of CO_2 uptake. However, the strength improvement is more related to water remained in carbonated samples. It was found that samples for 1 hour treatment possessed relative high compressive strengths after 28 days shown in Figure 4.8, but didn't exceed the strength of its hydration

reference. This might have occurred due to the loss of binding capacity in the long term, which resulted from preferential calcium carbonate formation at the early stage of cement hydration. It was proposed that the higher the content of carbonated products the more the negative influence on the strength (Janotka 2000). Therefore, it might be possible for 30-minute carbonated samples to achieve the highest compressive strength in the long term. To summarize, 28 day compressive strength of carbonated samples were dependent not only on content of CO_2 uptake but also on mass of evaporated water during carbonation. It is therefore suggested that carbonation degree could be controlled to achieve certain CO_2 capture with desired strength in the long term.

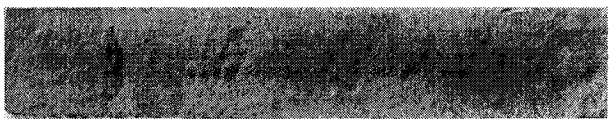
4.1.3 Qualitative Depth of Carbonation

Illustrated in Figure 4.9, Figure 4.10, Figure 4.11 and Figure 4.12 are qualitative depth of carbonation from four batches for 2-hour carbonation (P5CW), 1-hour carbonation (P7CW), 30-minute carbonation (P8CW) and 4-day carbonation (P6C). Immediately after spraying phenolphthalein indicator solution, similar colour patterns were obtained for samples immediately treated with CO_2 for 2 hours, 1 hour, 30 minutes and 4 days. A thin outer most surface layer was found to remain colourless, indicating a pH value less than 9. There then existed a band of purple, followed by another colorless band in the middle and finally a purple region in the core. The change from colourless to purple indicted a pH value greater than 9 (RILEM 1988). It should be noted that difference of CO_2 uptake, which was dependent on various exposure time, couldn't be demonstrated by colour patterns. Subsequent hydration for 4 and 28 days after carbonation resulted in similar patterns of changing from colourless to purple in some or most part of the cross section in all three cases. It could be inferred that further hydration occurred and pH of pore solution was recovered to certain degree. The colour pattern of carbonated samples after 28 day hydration did not display uniformly purple in fractured section, while purely purple was observed in entire fracture surface of reference hydration sample shown in Figure 4.13.

Phenolphthalein indicator solution is usually used to quantify carbonation depth of hardened concrete. Hardened cement paste with certain thickness can be totally carbonated and full carbonation is able to be identified by this phenolphthalein test (Anstice *et al* 2005). Because measurement is affected by the time after application of indicator solution, it is recommended to perform 24 hours after indicator spraying (RILEM 1988). For carbonated fresh cement paste compacts, although apparent colourless surface layer could be found immediately after spraying, colourless pattern might not be maintained after 24 hours, which was shown in Figure 4.11(a). There was the clear boundary between non-carbonated and carbonated areas became more difficult to identify at that time. This might have occurred due to continuous hydration in fresh carbonated samples. By comparison, colour patterns of carbonation depth 24 hours after spraying will be relative stable if maximum degree of hydration of matured samples is insured before carbonation. It is therefore suggested that phenolphthalein solution indicator may not be suitable on assessing early-age carbonation effect on pH value of carbonated fresh cementitous products. A more reliable PH quantification is necessary in detecting the pH change.



(a) Immediately after 2 hour carbonation (P5CW0)

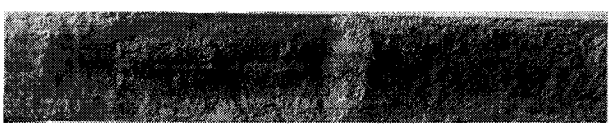


(b) After 2 hour carbonation and 4 day hydration (P5CW4)

(c) After 2 hour carbonation and 28 day hydration (P5CW28)

Figure 4. 9: Qualitative depth of carbonation of cement paste compacts after 2 hour carbonation (0.15MPa) and hydration up to 28 days in water

(a) Immediately after 1 hour carbonation (P7CW0)

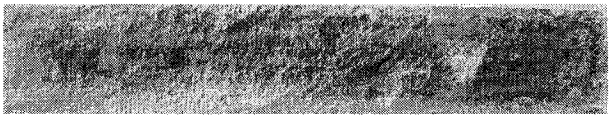


(b) After 1 hour carbonation and 4 day hydration (P7CW4)

(c) After 1 hour carbonation and 28 day hydration (P7CW28)

Figure 4. 10: Qualitative depth of carbonation of cement paste compacts after 1 hour carbonation (0.15MPa) and hydration up to 28 days in water

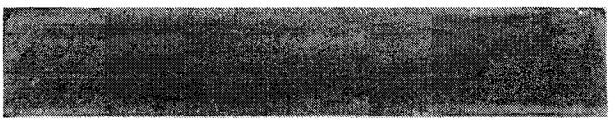
Immediately after spraying indicator solution



24 hours after spraying indicator solution

(a) Immediately after 30 minute carbonation (P8CW0)

(b) After 30 minute carbonation and 4 day hydration (P8CW4)



(c) After 30 minute carbonation and 28 day hydration (P8CW28)

Figure 4. 11: Qualitative depth of carbonation of cement paste compacts after 30 minute carbonation (0.15MPa) and hydration up to 28 days in water

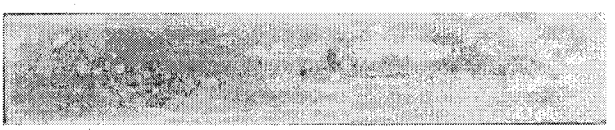
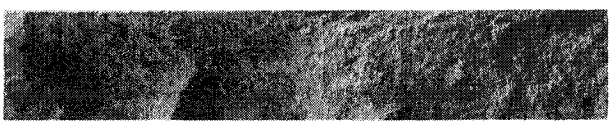


Figure 4. 12: Qualitative depth of carbonation of cement paste compacts after 4 day carbonation (0.15MPa) in moist chamber (P6C)



After 28 day hydration (P9HW28)

Figure 4. 13: Qualitative depth of carbonation of cement paste compacts after hydration up to 28 days in water

4.1.4 pH of Pore Solution

It is widely accepted that carbonation of concrete decreases the pH value of pore solution of concrete at which the passive film on reinforcing steel surface will be destroyed allowing the steel to corrode at a certain rate. Most of the previous carbonation corrosion studies had focused on the effect of weathering carbonation on hardened concrete by accelerated tests. pH value of pore water phase would drop below 9.0, if the matured concrete was totally carbonated (CEB 1988). Based on this understanding, application of early-age carbonation technology is usually confined to cement and concrete products without steel reinforcement. As a matter of fact, the carbonation degree of cement paste compacts with 2-hour treatment is about 25%, which is determined based on quantity of CO_2 uptake. Then, if pH of pore solution is not less than 11.5 (Bentur *et al* 1999) and becomes stabilized at certain age, carbonation corrosion might not be serious and carbonation could be even considered for accelerated curing of reinforced precast concrete. Furthermore, carbonated surface could be achieved with little effect on the core by controlled early-age carbonation. This treated surface with much reduced diffusion coefficient might be also beneficial serving as an anti-carbonation barrier to prevent atmospheric carbonation in service (Sanjuán and Olmo 2001). Therefore, early-age carbonation could be used for reinforced pre-cast concrete products. For this purpose, effect of early-age carbonation on pH of cement paste is to be examined in this thesis.

pH measurement of pore solution was performed on carbonated cement paste using suspension solution method described in section 3.4.6. pH values monitored under 2 hour carbonation and subsequent hydration are presented in Figure 4.14 and Figure 4.15. pH values of the surface layer were reduced to 11.97-12.06 immediately after 2-hour carbonation treatment and those in the core were observed to be 2% higher as the maximum. The discrepancy might be attributed to combined experimental variations caused by carbonation curing, powder sample preparation and pH measurement. pH values gradually increased with subsequent hydration both in water and in sealed bags. Up to 28 days, pore solution pH values of carbonated samples were slightly recovered but did not reach to those of hydrated samples.

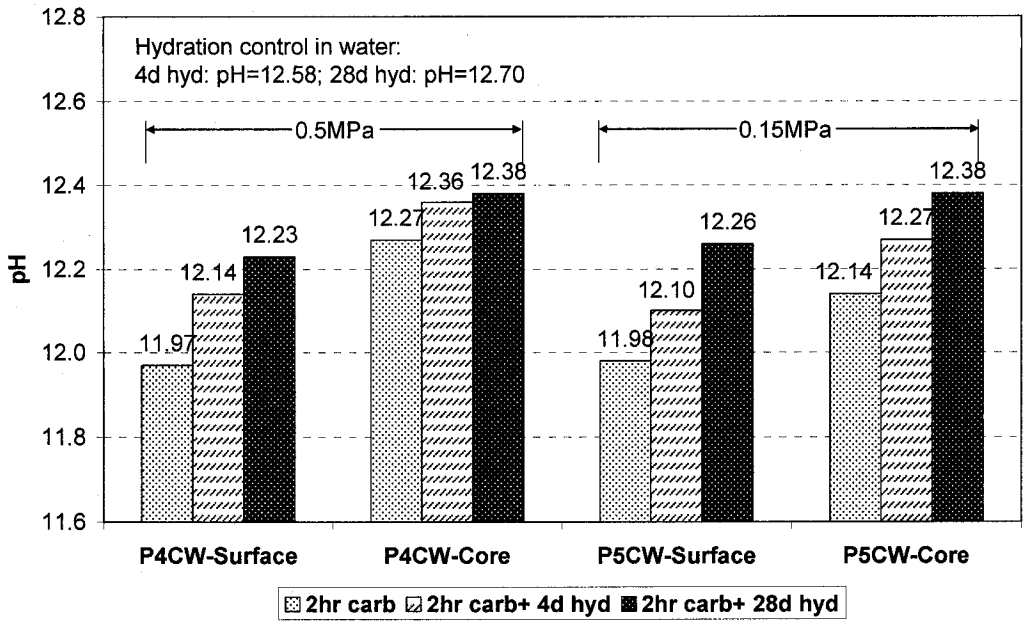


Figure 4. 14: pH of pore solution of carbonated cement paste compacts up to 28 days in water

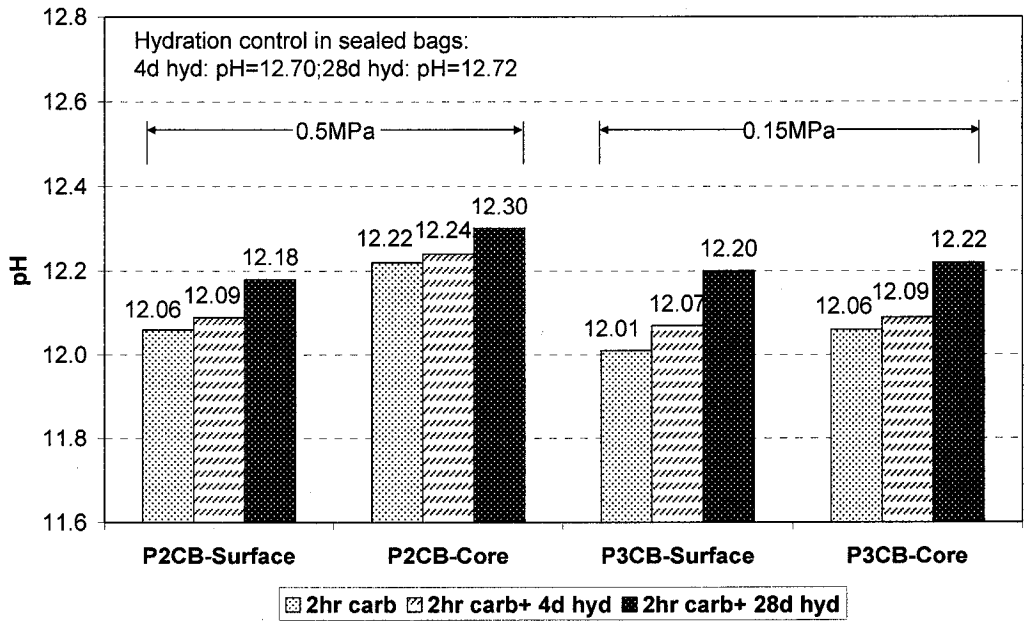


Figure 4. 15: pH of pore solution in carbonated cement paste compacts up to 28 days in sealed bags

Gas pressure effect was not noticeable for pH change, because gas pressures of both 0.5MPa and 0.15MPa resulted in similar pH values immediately after carbonation and after 28-day hydration. Curing in sealed bags didn't lead to greater pH restoration since about 50% mixing water was evaporated due to early-age carbonation, which might limit progressive hydration. Moreover, carbonated samples, which were cured in tap water for better hydration, possessed only slightly increased pH than those of samples hydrated in sealed bags. This might be attributed to reduced percentage of water absorption or decreased binding capacity of water and anhydrated materials due to carbonation products described in section 4.1.2.3.

Typical pH value change in curing water is shown in Figure 4.15. The hydrated reference cement paste compacts were placed in moisture chamber in the first 24 hours in order to achieve sufficient strength prior to water curing. The specimens carbonated before hydration were cured in water immediately after treatment with CO_2. On the one hand, it was indicated that calcium hydroxide produced during hydration diffused through the pores to the surface of the samples, resulting in a pH increase in curing water. It was also observed that more calcium hydroxide was produced and thus leached from hydrated samples, leading to a higher pH value of curing water. On the other hand, pH changes of water for curing carbonated and non-carbonated samples showed a similar profile with a significant increase in 4 days and gradual increment to get almost stabilized up to 28 days. It was found that at equilibrium pH of curing water reached 11.76 for carbonated samples and 12.88 for hydrated reference. It is interesting to notice that they were comparable with pH measurement from suspension solution of two different batches.

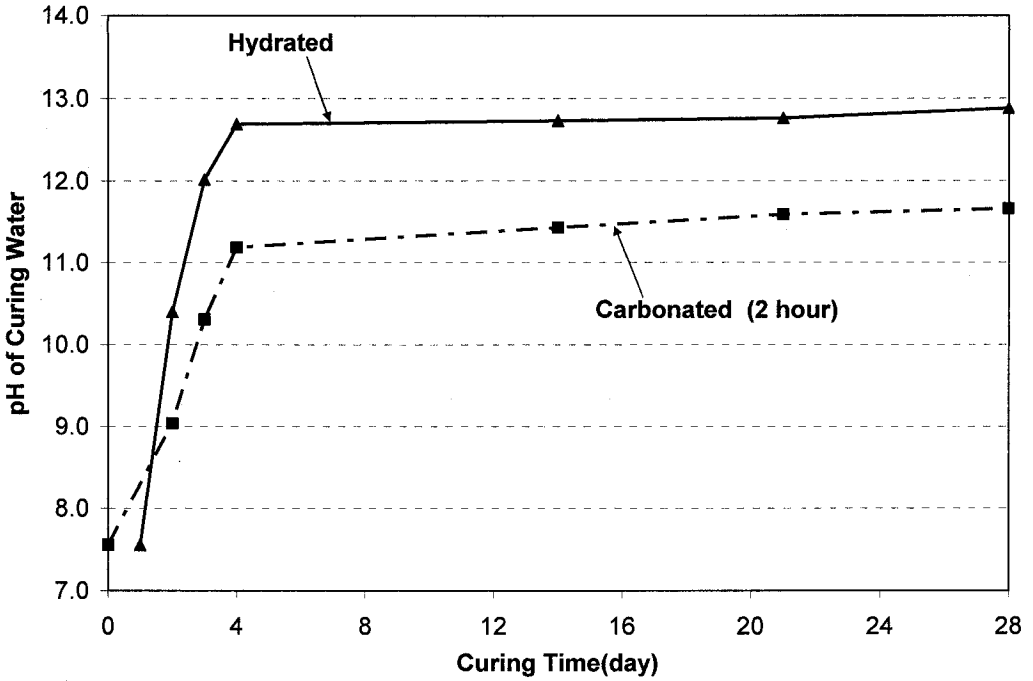


Figure 4. 16: Typical pH profile of curing water for hydration of carbonated and non-carbonated cement paste compacts

Figure 4.17 shows the effect of carbonation time on pH of cement paste carbonated by 2 hours, 1 hour and 30 minutes. It was also observed that the core possessed higher pH of pore solution than that of the surface in all three batches. Shortening 2 hour treatment to 1 hour resulted in 1. 6% decrease in CO_2 uptake (see Table 4.3), 1.5% and 0.8% decrease in pH for the surface and the core respectively. Further reduction of exposure time to 30 minutes resulted in less 5.6% CO_2 uptake (see Table 4.3), 2.4% and 2.7% reduction in pH for surface and the core respectively. pH values of pore solution in both the surface and the core were recovered gradually to different degree up to 28 days due to further hydration. After 28-day subsequent hydration, samples carbonated for 2 hours had 2.2% and 0.9% pH increase in the surface and core respectively, and possessed lowest pH of pore solution for both surface and core of all three cases. Samples carbonated for 1 hour had 1.7% and 2.6% increase in pH of the surface and in the core respectively up to 28 days, while there were 1.1% and 0.9% pH increase in the surface and core respectively for samples treated for 30 minutes. It was found that pore solution pH of the core in

cement paste samples carbonated by 60 minutes or 30 minutes was compared to that of hydrated control samples. This could be attributed to higher remaining water content after carbonation and subsequent hydration due to less degree of carbonation.

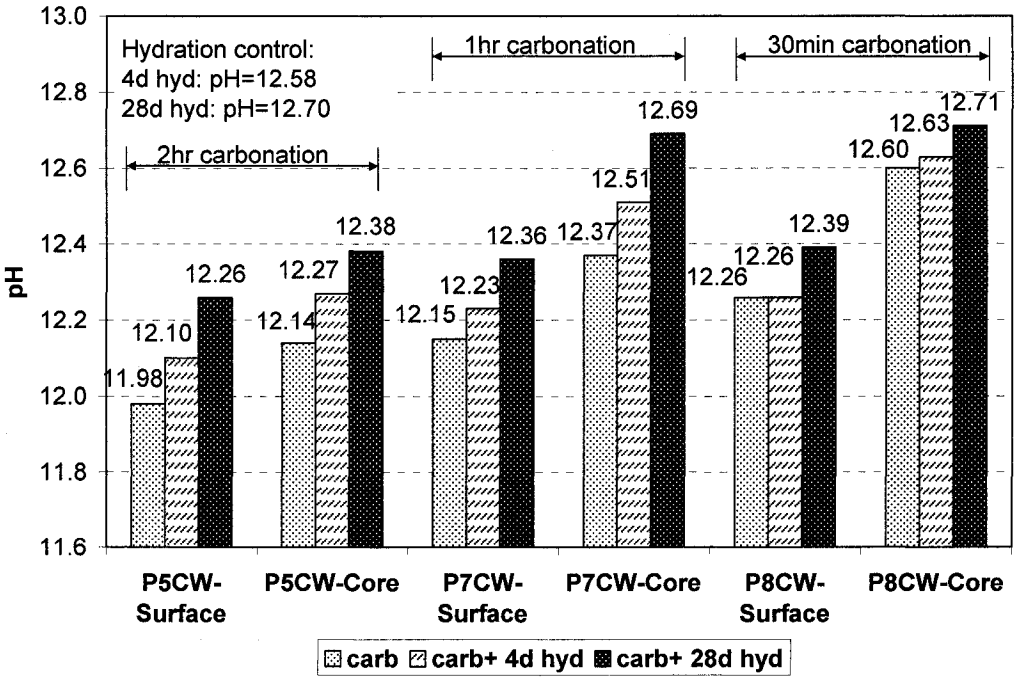


Figure 4. 17: Effect of carbonation time on pH of carbonated cement paste compacts (at 0.15 MPa) up to 28 days in water

A linear correlation between average CO_2 uptake and average pH of carbonated cement paste compacts is presented in Figure 4.18. The average pH refers to mean pH value of the surface and in the core. The average CO_2 uptake is the mean CO_2 content of the surface and core respectively determined by constant-temperature pyrolysis techniques (PT) and shown in Table 4.3. It is clear that pH value of immediately carbonated cement paste was correlated with CO_2 uptake. In other word, the higher the CO_2 absorbed the lower the pH. Due to subsequent hydration up to 28 days, the linear curve shifted above but with different slopes.

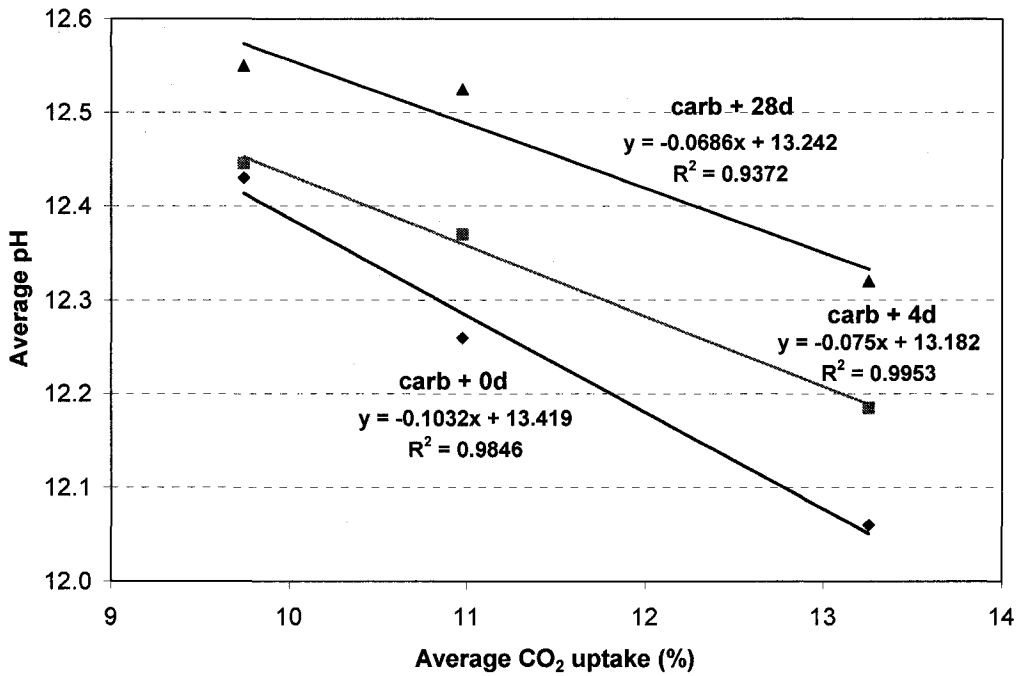


Figure 4. 18: Correlation between average CO_2 uptake and average pH of carbonated cement paste compacts

Pore solution pH of cement paste compacts after 4 days with different carbonation and hydration treatments is presented in Table 4.6. It was indicated that prolonged treatment with CO_2 for continuous 4 days (Batch P6C) did not lead to much decreased pH value. This might be due to simultaneous carbonation and hydration in moist environment. pH value of samples in batch P6C continuously carbonated for 4 days was comparable to those of samples through 2-hour carbonation followed by 4 day hydration.

Table 4. 6: pH of pore solution phase of cement paste compacts with different treatments after 4 days

Batch	Carbonation Treatment and Hydration	pH	
		Surface	Core
P6C	96 hour carbonation(0.15MPa) with extra moisture	11.99	12.21
P3CB4	2 hour carbonation(0.15MPa) + 4 day hydration in sealed bags	12.07	12.09
P5CW4	2 hour carbonation(0.15MPa)+ 3 day hydration in water+ 1 day hydration in the air	12.10	12.27

To summarize, pH of pore solution in cement paste compacts exposed to 2-hour carbonation was reduced to about 12.0. This was corresponding to a 25% carbonation degree after 2-hour CO_2 injection. Similar observation was found that the pH value of wood-cement composites was reduced to 11.7 after 30 minute carbonation (Qi 2005). Although subsequent hydration either in water or in sealed bags was unable to lead to complete pH restoration, the slight increase in pH after carbonation guaranteed a value, greater than 11.5 for safeguard of the passive film on the steel surface to avoid corrosion hazard. It is also suggested that the pH values of pore solution in cement and concrete might be adjusted through a controlled carbonation process. The pore solution pH of the core could be restored to catch up with that of hydrated samples if exposure time is shortened to 1 hour or 30 minutes. It also seemed impossible to promote full carbonation at early age, especially when hydration was taking place simultaneously. Therefore early age carbonation is totally different from weathering carbonation which is capable of reaching full carbonation of hardened concrete and neutralizing the pH of pore solution.

4.1.5 X-ray Diffraction

X-ray diffraction pattern analysis was performed on selected cement paste samples to examine the phases produced and consumed during carbonation curing. Moreover, XRD patterns of carbonated samples followed by subsequent hydration were also analyzed in order to identify any hydration products formed after treatment with CO_2.

The typical XRD patterns are shown in Figures 4.17 for hydrated cement paste reference. C_3S peaks were more significantly reduced through water curing in comparison through curing in sealed bags, suggesting a higher hydration degree. It was also evident by compressive strength as high as 83.9 MPa of water cured cement paste, far exceeding strength of hydrated samples cured in sealed bags and all carbonated samples.

The typical XRD patterns of 2-hour carbonated samples are shown in Figures 4.18. The analysis indicated that calcium carbonates in the form of calcite and aragonite were the primary products after 2-hour carbonation curing. Comparison of C_3S and C_2S in

carbonated and non-carbonated cement paste compacts suggested that although a fraction of calcium silicate phases were consumed a large number of peaks still existed which was in agreement with the carbonation degree of 25%. There was also no evidence to show any formation of hydration products immediately after carbonation curing. Furthermore, no significant differences were observed in XRD patterns of the surface and core samples. Same phenomenon was observed by Chad (2006). After 2 hour carbonation and 28 day hydration, strong calcite peaks were still dominant indicating that carbonation curing converts the gaseous carbon dioxide to solid calcium carbonates mainly in the from of stable calcite. For carbonated samples either cured in water or in sealed bags, XRD patterns revealed calcium hydroxide peak only at 47.1° for both the surface and core samples. For the core sample cured in water, ettringite lines occurred at 32.4° and 56.4° in the position where there were interfaces with C_2S and C_3S. For non-carbonated samples hydrated in conventional curing conditions, XRD spectra revealed several calcium hydroxide peaks with the two strongest each at 18.1° and 34.1°. Also, ettringite peaks at 23.1° and 32.3° were detected for the sample cured in water.

It is, therefore, conclusive that 28 day hydration following 2-hour carbonation could be impeded. Hydration was accelerated in 2-hour carbonation with a compressive strength comparable to that by subsequent 28-day hydration. This was also consistent with observations that pH restoration of carbonated samples was not significant in subsequent 28 day hydration and the pH value was still lower than hydrated references.

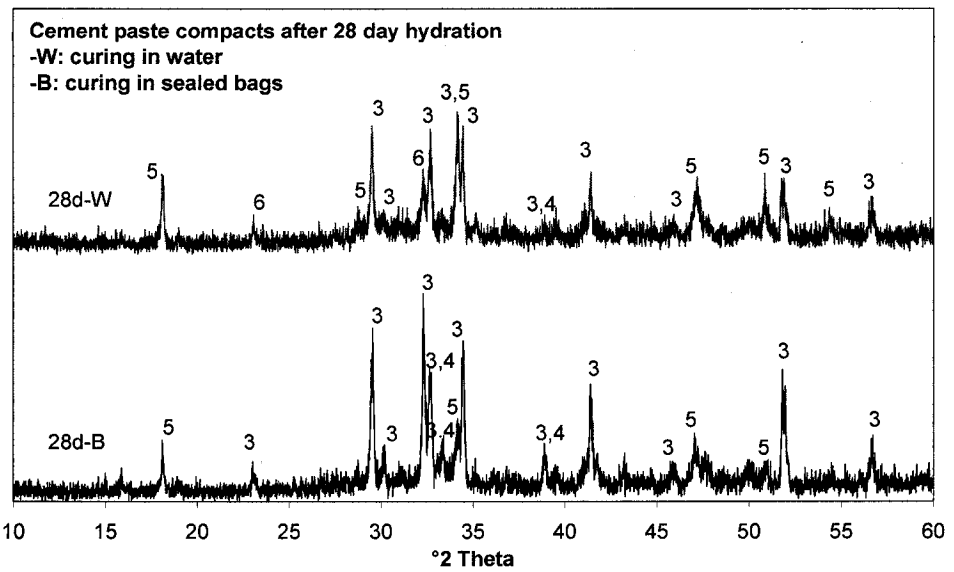


Figure 4. 19: XRD patterns of cement paste compacts after 28 day hydration: (1) calcite, (2) aragonite, (3) C_3S, (4) C_2S, (5) calcium hydroxide, (6) ettringite

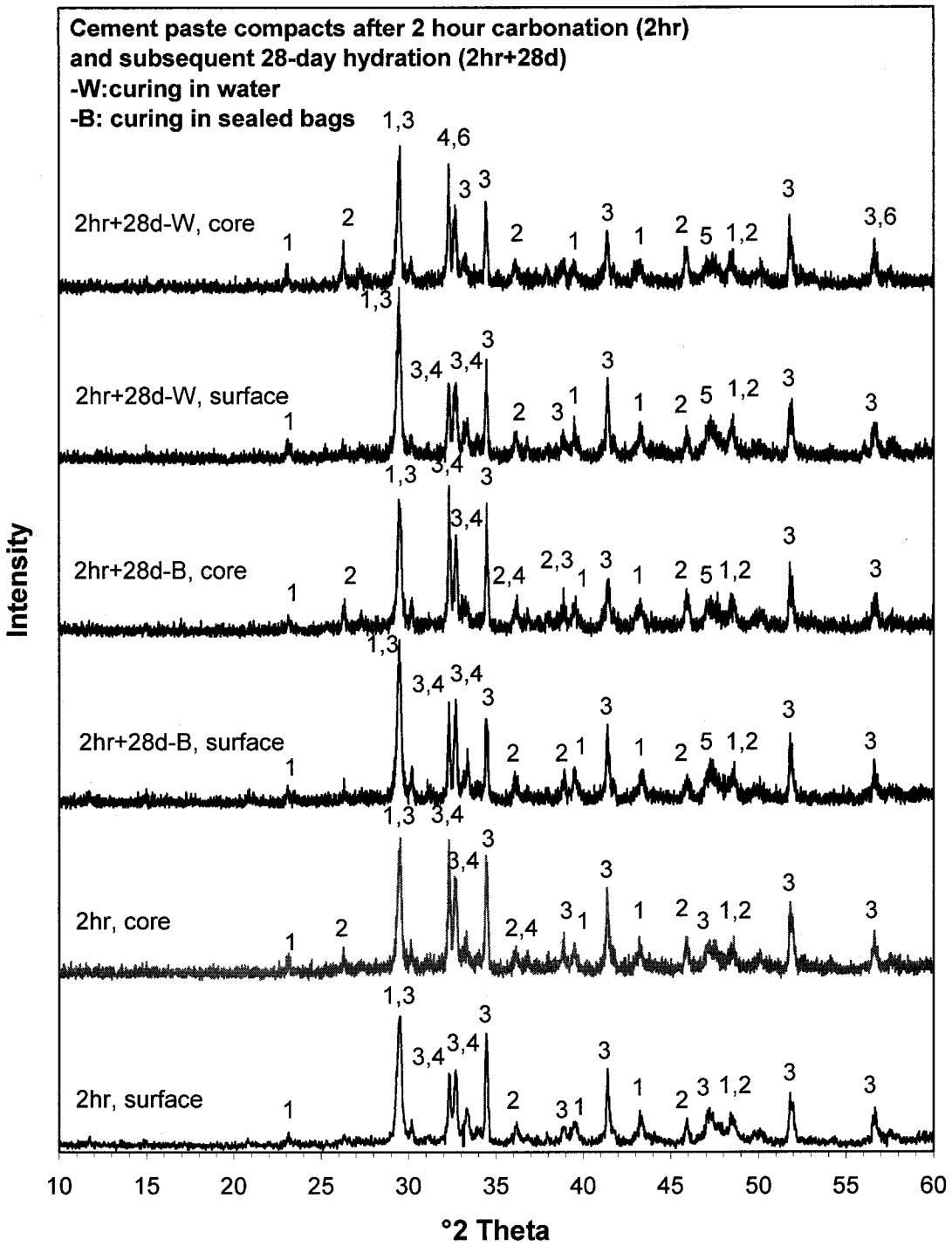


Figure 4. 20: XRD patterns of cement paste compacts after 2 hour carbonation and subsequent 28 day hydration: (1) calcite, (2) aragonite, (3) C_3S, (4) C_2S, (5) calcium hydroxide, (6) ettringite

4.2 Performance of Carbonated Concrete Compacts

It was found in section 4.1 that: 1) 28-day compressive strength of 2-hour carbonated cement paste samples was 50% higher than that of hydrated reference cured in sealed bags; 2) 28-day compressive strength of 2-hour carbonated cement paste samples was 30% lower than that of hydrated reference cured in water; 3) The compressive strength improvement of 2-hour carbonated samples was not significant during subsequent hydration. It is therefore interesting to know if the same results can be obtained from concrete products, such as masonry units and paving stones. It was also noticed that water loss during carbonation curing might be a limiting factor for subsequent hydration. Consequently, preventing water from expelling during carbonation is essential to the further hydration of carbonated products. Two approaches were adopted in carbonation of concrete products in order to deal with the problem associated with water loss in carbonation reaction: 1) use of pre-soaked lightweight aggregates (LWA) as internal curing agent and 2) use of chemical admixture- Solvitose FC 100.

4.2.1 Carbonation Curing Behaviour

Carbonation curing results of concrete compacts are presented in Table 4.7. Six concrete samples in each batch were simultaneously carbonated at a pressure of 0.15MPa for 2 hours. The maximum temperatures were in the range of 53°C to 60°C, about 48% to 54% of the peak temperature achieved in cement paste compacts carbonated under similar conditions. A lower peak temperature implied a less exothermic reaction because of the less cement content in concrete compact.

Batch C3CB was a limestone concrete carbonated for 2 hours and hydrated in 28 days, and was used as reference to determine water loss during carbonation reaction. Compared to cement paste compacts, less water loss was observed in concrete compacts because of lower cement content (19%) used during carbonation reaction.

In batches C4CB and C5CB, limestone was intended to be partially replaced by pre-soaked LWA (see Table 3.8) to examine the influence of water and investigate the effect of pre-soaked LWA as an internal curing on the strength development. Based on content of water loss during reaction in batch C3CB, same amount of water was used in batch C4CB. The water of batches C4CB and C5CB was divided into two parts. The first part was used as mixing water and the other as an internal curing agent carried by LWA. The ratio of mixing water to cement is defined as effective water to cement ratio. It was observed that lower effective water to cement ratio of 0.20 led to about 4.3% higher water loss and 1.9% more CO_2 uptake in comparison to carbonated reference batch C3CB. This might have occurred due to the fact that carbonation reaction was promoted by decreased amount of mixing water, leading to a slightly more reaction. In batch C5CB, the effective water to cement ratio was the same as in batch C3CB. Additional water at a w/c=0.06 was carried by LWA as water loss compensation. It was found that extra moisture resulted in 5.0% less water evaporation and 1% less mass gain. These results revealed that carbonation reaction could be hindered with more water soaked by LWA while keeping constant mixing water content.

Furthermore, certain amount of starch-based chemical admixture (Solvitose FC 100) at 0.1% and 2% of cement weight was employed in C6CB and C7CB to investigate its effect on preventing water from evaporating during carbonation reaction. It was found that Solvitose FC100 could not stop water evaporation however it did promote CO_2 uptake. Sovitose FC 100 at 2% only led to 2.1% higher mass gain but had no effect on water loss.

Similar to cement paste compacts, linear relationship of mass gain with respect to water loss in carbonation of concrete compacts was observed and illustrated in Figure 4.21. It should be noted that the batch C7CB with excessive content of Solvitose FC 110 was excluded. It indicated that for each mole water loss, there is 0.80 mole carbon gain for those carbonated samples. In exothermic carbonation process, larger quantity of water evaporation led to more pores inside the concrete compacts, resulting in more CO_2

diffusion and thus higher mass gain. It is suggested that carbonation control could be associated with the water loss control during CO_2 treatment.

Table 4. 7: Carbonation behaviour for concrete compacts

Batch	Peak Temperature (°C)	Water Loss[1] (%)	WG[2] (%)	MC[3] (%)	Initial w/c[4]	Final w/c[5]
C3CB	54	23.7	9.6	12.2	0.26	0.20
C4CB	60	28.0	11.6	14.0	0.20[6]+0.06[7]	0.19
C5CB	53	18.7	8.7	10.7	0.26[6]+0.06[7]	0.26
C6CB	56	25.0	10.4	13.4	0.26	0.19
C7CB	56	24.7	11.8	14.0	0.26	0.19

Note:

1 Ratio of water evaporated to total mixing water
2 Percentage of weight gain calculated from Equation 3.3
3 Percentage of CO_2 mass gains from mass curve readings
4 Ratio of initial water content to cement content before carbonation
5 Ratio of remaining water content after carbonation to cement content
6 Effective water cement ration or ratio of mixing water content to cement content
7 Ratio of water content absorbed by LWA to cement content

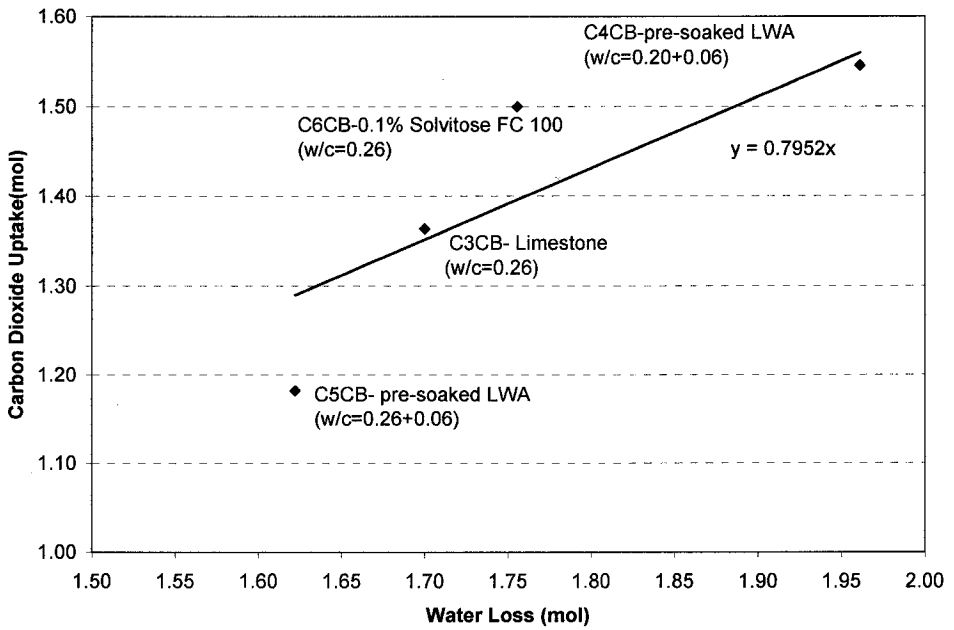


Figure 4. 21: Relationship between water loss and CO_2 uptake in carbonation of concrete compacts

4.2.2 Mechanical Performance

Flexural and compressive strength results for concrete compacts are summarized in this subsection. All strength results presented are average of three samples and the standard deviations are also reported. Mechanical performances of carbonated concrete compacts were studied right after 2-hour carbonation and after 28-day hydration in sealed bags to study the internal curing effect and the chemical admixture effect.

4.2.2.1 Effect of Pre-soaked LWA

The batch C3CB is regarded as carbonated reference limestone concrete. Strength results for carbonated concrete compacts in this batch as well as its hydrated reference are shown in Table 4.8. Flexural strength of samples immediately carbonated could be compared with that of hydrated ones. However, a reduction in flexural strength by 32% was observed up to 28 days. 2-hour carbonated samples in the batch C3CB possessed a compressive strength as 9.7 MPa and further hydration led to an increase by 38.14% at 28 days to 13.4 MPa. However, compared to hydration reference which had possessed the strength of 10.2 MPa, carbonated concrete was 17% less strong. It was clear that both flexural and compressive strengths of conventionally hydrated concrete compacts exceeded those of concrete specimens after 2-hour carbonation following 28 days. This was likely due to loss of water in carbonation reaction. A similar strength reduction was observed on compressive strength of carbonated cement paste compacts subsequently hydrated in water.

Table 4. 8: Strength results for concrete compacts of carbonated and hydrated reference batches

Limestone Concrete		Flexural Strength (MPa)	Compressive Strength (MPa)
Batch	Treatment		
C3CB	2hr carbonation	1.9±0.4	9.7±0.7
	2hr carbonation + 28d hydration	1.2±0.3	13.4±0.7
C1HB	28d hydration	1.9±0.1	16.2±0.2

In order to solve the problem observed as internal curing agent to compensate for the water loss and in batch C3CB, pre-soaked LWA was used in the batches C4CB and C5CB. Strength results for these two batches are shown in Figure 4.22. The flexural and compressive strength of samples immediately after carbonation in batch C4CB (w/c=0.20+0.06) were 25.4% and 7.5% higher than those of batch C5CB (w/c=0.26+0.06). This was possible because of the higher CO_2 uptake in batch C4CB. The flexural strength improvement of carbonated samples using pre-soaked LWA was significant after 28 days. Carbonated samples in the batch C4CB possessed the highest flexural strength after 28 days, which was more than doubled as initial strength right after treatment with CO_2. In the batch C5CB, carbonated specimens had 86% increase of flexural strength up to 28 day hydration. It was also found that carbonated samples in batch C4CB had 32.9% higher flexural strength than samples in batch C5CB up to 28 days, in spite of lower water to cement ratio after carbonation. It seemed that flexural strength improvement of carbonated concrete samples was more related to quantity of CO_2 uptake through carbonation curing. Carbonated samples in both batches had 98% and 15% higher 28-day flexural strength respectively than that of their hydrated control batch.

The compressive strengths of carbonated samples in batches with pre-soaked LWA were found to increase about 86.6% and 113.4% respectively after 28 days, both of which were higher than their of its hydrated reference batch. It was also observed that of the two batches carbonated samples in batch C5CB possessed 3.8% higher compressive strength after 28-day hydration. It seemed that those carbonated samples with higher initial strength did not develop strength proportionally in the subsequent hydration. This phenomenon was also observed in cement paste compacts and could be explained by the remaining water content. Therefore, compressive strength development of carbonated concrete samples might be more dependent on ultimate water to cement ratio after carbonation reaction.

Investigating the effect of pre-soaked LWA as an internal curing agent, strength development of carbonated concrete specimens was evaluated. As mentioned above,

development of both flexural and compressive strength of carbonated samples was significant in batches (C4CB and C5CB) using pre-soaked LWA. Furthermore, 28-day strengths of carbonated concrete did exceed those of its hydration reference. In two batches using pre-soaked LWA, compressive strengths of samples right after carbonation were found to be 17.8% and 25.5% lower than that of carbonated reference batch (C3CB) without pre-soaked LWA. However, 28-day compressive strengths of samples in batches C4CB and C5CB were about 11.0% and 15.2% higher than that of carbonated concrete without LWA (C3CB), although they were still lower than that of hydrated concrete (C1HB). It seemed that pre-soaked LWA acted as the uniformly distributed water resource to help achieve better internal hydration. It is therefore conclusive that use of pre-soaked is an effective approach to compensate for water loss and promote internal curing, although application of pre-soaked LWA inevitably may lead to certain reduction in strength.

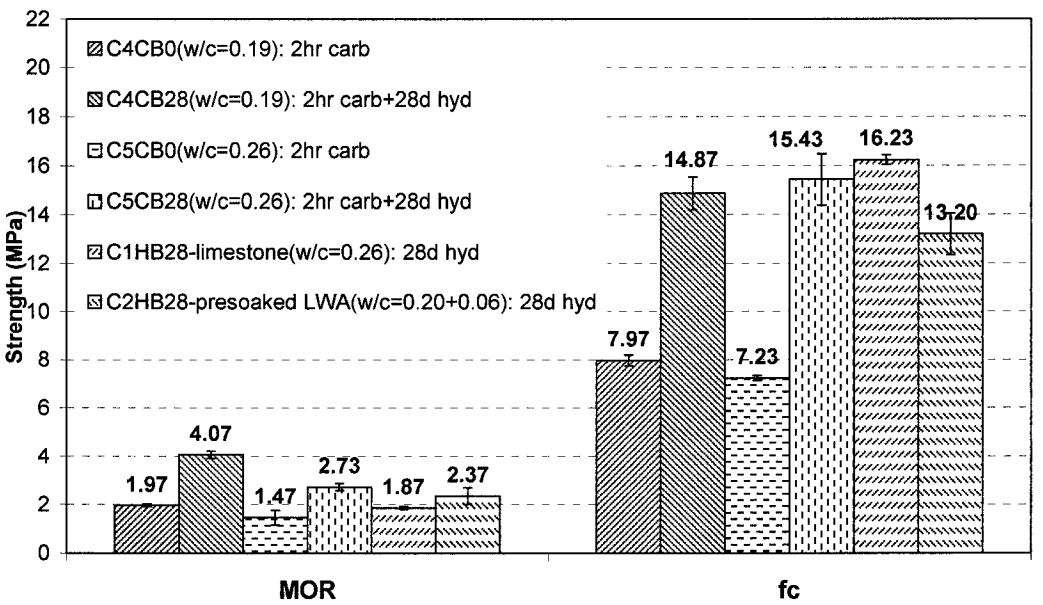


Figure 4. 22: Effect of pre-soaked LWA as an internal curing with on strength development of carbonated concrete compacts up to 28 days in sealed bags

Note: For batches C4CB and C5CB, final w/c (see Table 4.7)

4.2.2.2 Effect of Chemical Admixture

Effect of starch-based chemical admixture (Sovitose FC 100) on strength results of concrete compacts is summarized in Figure 4.23. Carbonated samples in the batch C6CB with 0.1% Solvitose possessed 19.8% lower initial flexural strength than that of its carbonated reference, while their strength improvement was found to be the most significant and became the highest after 28 days. The batch C7CB with 2% Solvitose had the lowest MOR immediately after carbonation. Although the development of flexural strength in this batch was observed to be about 60%, it was only slightly higher than that of carbonated reference batch after 28 days. It was observed that flexural strength of carbonated samples in batch using 0.1% Solvitose did exceed that of hydrated control batch up to 28 days. Too much admixture resulted in a detrimental impact on both initial and 28-day strength.

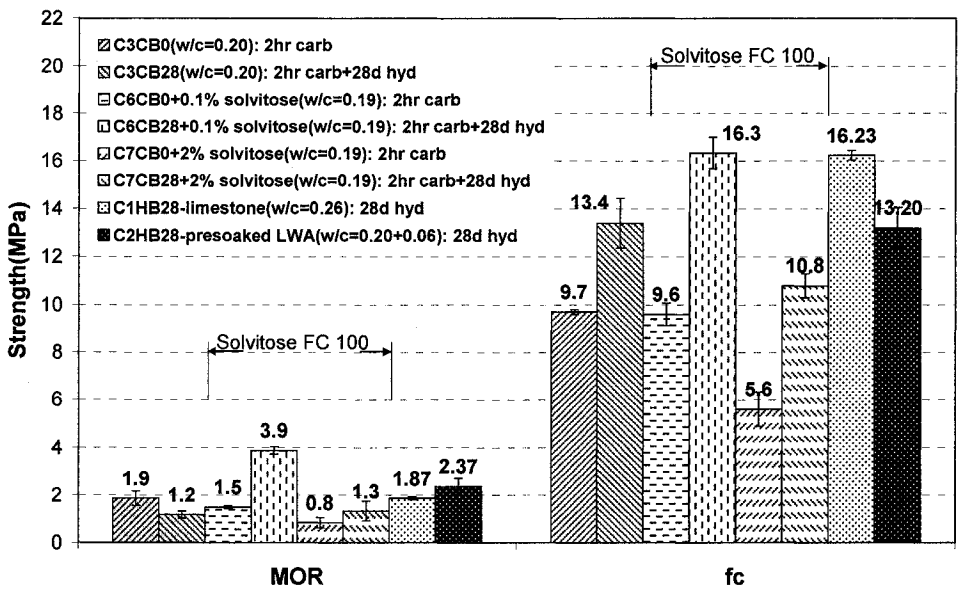


Figure 4. 23: Effect of Solvitose FC 100 on strength development of carbonated concrete compacts up to 28 days in sealed bags

Note: For batches C3CB, C6CB and C7CB, final w/c (see Table 4.7)

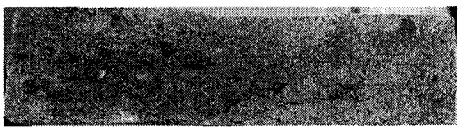
It was observed that samples immediately treated by CO_2 in batch with 0.1% Solvitose possessed similar compressive strength to that of carbonated reference batch. Carbonated samples in this batch had 70.1% strength gain up to 28 days, which was 21.9% higher than that of carbonated reference batch. Furthermore, 0.1% Solviotse led to the highest 28-day strength slightly exceeding that of hydrated control batch. It was indicated that 0.1% Solvitose might not lead to great effect on compressive strength right after carbonation curing, however its contribution to 28-day compressive strength could be very significant. Batch C7CB with 2% Solvitose had the lowest compressive both immediately after carbonation and after 28 days. Although compressive strength development in batch C7CB was observed to be the greatest, after 28 days it was about 19% and 34% lower than that of its carbonated reference batch and hydrated reference batch respectively. It was inferred that compressive strength right after carbonation and after 28 days couldn't benefit from using of excessive admixture.

To summarize, water loss is again identified as one of the factors limiting subsequent hydration and strength improvement of carbonated samples. Based on internal curing concept, two batches were attempted by using pre-soaked LWA to compensate for moisture evaporated in carbonation reaction. Contrary to the phenomenon found in the batch without any treatment that strength of carbonated samples couldn't catch up with that of hydrated ones after 28 days, both of the batches with LWA possessed higher flexural and compressive strength, which were attributed to pre-soaked LWA as water reservoir for internal curing. Thus, pre-soaked LWA can be used as internal curing agent for better subsequent hydration and strength development of carbonated concrete samples. Solvitose FC 100, a starch-based chemical admixture, was initially expected to reduce water evaporation during carbonation reaction, whereas little influence was observed with either high and low dosage. Content of Solvitose at 0.1% might have a great contribution to strength improvement in both flexural and compressive strength of carbonated specimens in 28 day hydration.

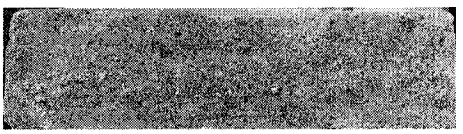
4.2.3 Qualitative Depth of Carbonation

Phenolphthalein indicator test was performed to qualitatively evaluate early-age carbonation depth of concrete compacts. Pictures on qualitative carbonation depth of concrete specimens in different batches C3CB (without internal curing), C4CB (with internal curing, w/c=0.20+0.06) and C5CB (with internal curing and additional water at w/c=0.26+0.06) are shown in Figure 4.24, Figure 4.25 and Figure 4.26 respectively. For all immediately carbonated concrete compacts, there was some colourless region in the outer most surface layer surrounding the purple core. It seemed that the area of the colourless part was proportional to average CO_2 uptake of the samples presented in Table 4.7. Furthermore, area of purple region could become larger after 28 days due to further hydration. The change from colourless to purple indicated a pH value greater than 9.0. It could be therefore indicated that pH of pore solution was restored to some extent. However, the colour patterns also revealed that small colourless region could still remain after 28 days and did not become purely purple as shown in Figure 4.27 for samples after 28 day normal hydration.

By comparing colour patterns of immediately carbonated samples right after indicator spraying to 24 hours after testing, similar observation to that found in cement paste compacts was obtained. The border between carbonated and non-carbonated parts became ill-defined 24 hours after testing. Therefore, using phenolphthalein indicator solution to predict carbonation depth and corrosion hazard of fresh concrete does not seem suitable.

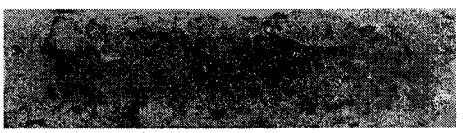


Immediately after spraying indicator solution



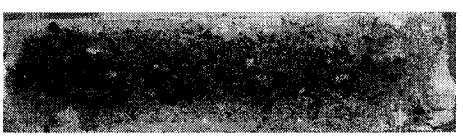
24 hours after spraying indicator solution

(a) Immediately after 2 hour carbonation (C3CB0)

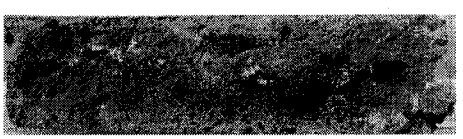


(b) After 2 hour carbonation and 28 day hydration (C3CB28)

Figure 4. 24: Qualitative depth of carbonation of concrete compacts (without internal curing) after 2 hour carbonation and 28 day hydration in sealed bags

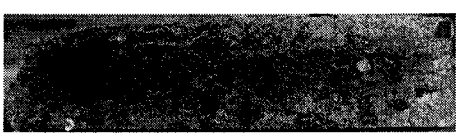


Immediately after spraying indicator solution



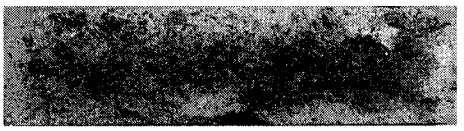
24 hours after spraying indicator solution

(a) Immediately after 2 hour carbonation (C4CB0)

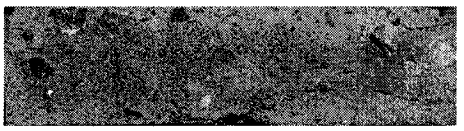


(b) After 2 hour carbonation and 28 day hydration (C4CB28)

Figure 4. 25: Qualitative depth of carbonation of concrete compacts (with internal curing, w/c=0.20+0.06) after 2 hour carbonation and 28 day hydration in sealed bags



Immediately after spraying indicator solution

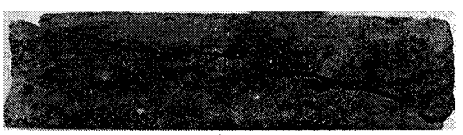


24 hours after spraying indicator solution

(a) Immediately after 2 hour carbonation (C5CB0)

(b) After 2 hour carbonation and 28 day hydration (C5CB28)

Figure 4. 26: Qualitative depth of carbonation of concrete compacts (with internal curing, w/c=0.26+0.06) after 2 hour carbonation 28 day hydration in sealed bags



After 28 day hydration (C1HB28)

Figure 4. 27: Qualitative depth of carbonation of concrete compacts (w/c=0.26) after hydration up to 28 days in sealed bags

4.2.4 pH of Pore Solution

For similar purpose of quantifying pore solution pH values of carbonated cement paste in subsection 4.1.4, an assessment was conducted on carbonated concrete compacts by using bulk powder in suspension solution. All pH values are compared with mass gain through carbonation curing and are present in Figure 4.28. Comparing to hydration reference, pore solution pH values of carbonated concrete compacts were reduced to the lowest of 11.8 in all five batches. This might be reasonable because the carbonation degree was no greater than 23%. It was observed that the concrete compact with a larger amount of CO_2 uptake possessed a lower pH of pore solution immediately after carbonation. pH recovery was very slight in further hydration process up to 28 days. Pore solution pH of carbonated concrete samples was still lower than that of their hydrated references after 28 day hydration.

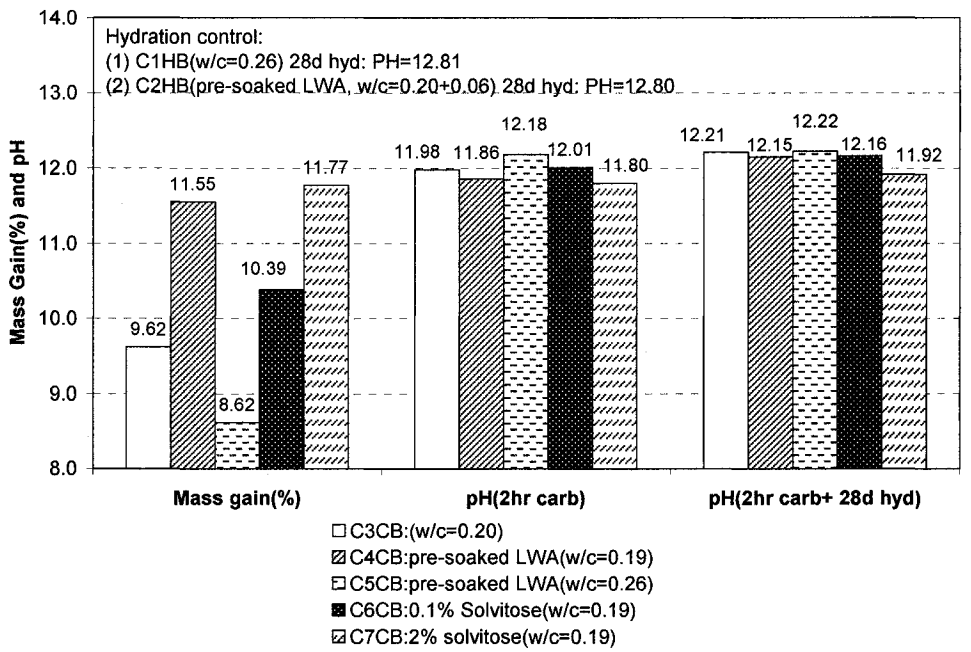


Figure 4. 28: Comparison between mass gain and pH of pore solution in concrete compacts after 2 hour carbonation and 28 day hydration in sealed bags

Note: For batches C3CB, C4CB, C5CB,C6CB and C7CB, final w/c (see Table 4.7)

4.3 Performance of Carbonated Precast Concrete

pH assessment of pore solution in carbonated cement paste and concrete compacts was conducted in the previous two subsections. It was observed that their pH values were still greater than 11.5, a threshold value under which corrosion is likely to occur. It therefore suggested that early-age carbonation curing can be applied for accelerated hardening of reinforced precast concrete. A study was carried out to make carbonation of fresh precast concrete available. Precast concrete samples with both normal aggregate and lightweight aggregate (LWA) were investigated. Furthermore, carbon dioxide uptake by precast concrete samples was evaluated as well as their properties immediately after carbonation curing and subsequent hydration.

4.3.1 Control of Water Loss before Carbonation Curing

To make fresh precast concrete as a new candidate product to sequester carbon dioxide, the following prerequisites should be taken into account:

- Sufficient workability should be ensured to make concrete readily compactable. As a result, some factors influencing workability of concrete should be taken into account: 1) water to cement ratio, 2) coarse/fine aggregate ratio, 3) aggregate/cement ratio, 4) maximum size of aggregate (Neville, 1995).
- Some water must be presented for the carbonation reaction to proceed, but excessive moisture drastically limits the reaction because saturation of pore system led to slow CO_2 diffusion into the concrete sample (Young *et al* 1974). Therefore, certain amount of moisture should be removed from fresh precast concrete samples, particularly from the surface, so that carbonation reaction can be available and progressive.
- Withdrawal of water from concrete cured in unsaturated air causes drying shrinkage. It was influenced by many factors, including water to cement ratio, aggregate content *etc*. Lightweight aggregate usually results in higher shrinkage because its lower modulus of elasticity offers limited restraint to the potential

shrinkage of the cement paste (Neville, 1995). The effect of early-age drying on shrinkage was not studied in this preliminary project.

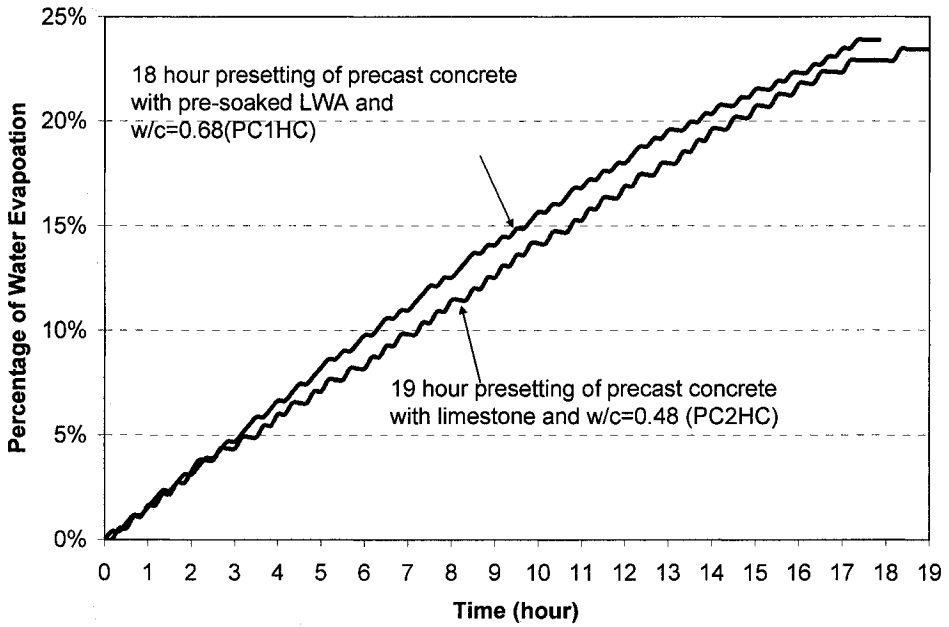


Figure 4. 29: Percentage of water evaporation during presetting for batch PC1HC and PC2HC

Based on the considerations mention above, several trials were performed before achieving desired workability with mix proportion proposed in Table 3.12. Duration of presetting and drying were attempted to remove certain quantity of water from fresh concrete samples. Prior to carbonation curing, precast concrete samples with pre-soaked lightweight aggregate (LWA) in batch PC1HC, were initially preset in moulds for 18 hours with one surface exposed to air (room temperature: 22°C, relative humidity = 65%), and then oven-dried at 50°C for 1 hour after demoulding. For concrete samples using limestone in batch PC2HC, 19 hour presetting was applied without further oven-drying. On the one hand, percentages of water evaporations (ratio of water evaporation during presetting to total water content) were recorded every 10 minutes by a digital balance with data acquisition system, and are shown in Figure 4.29. On the other hand, ultimate water loss after presetting, presented in Table 4.9, was also obtained by measuring the

weight difference before and after presetting. Besides, percentage of water loss (ratio of water evaporation to total water content) during oven-drying for batch PC1HC is shown in Figure 4.30.

Table 4. 9: Water loss of precast concrete during presetting

Batch	Initial w/c	Percent of Water Loss During Presetting Measured By Scale	Percent of Water Loss During Oven-Drying Measured By Scale	w/c Before Carbonation
PC1HC	0.48+0.20	21.7%	14.3%	0.44
PC2HC	0.48	22.8%	/	0.37

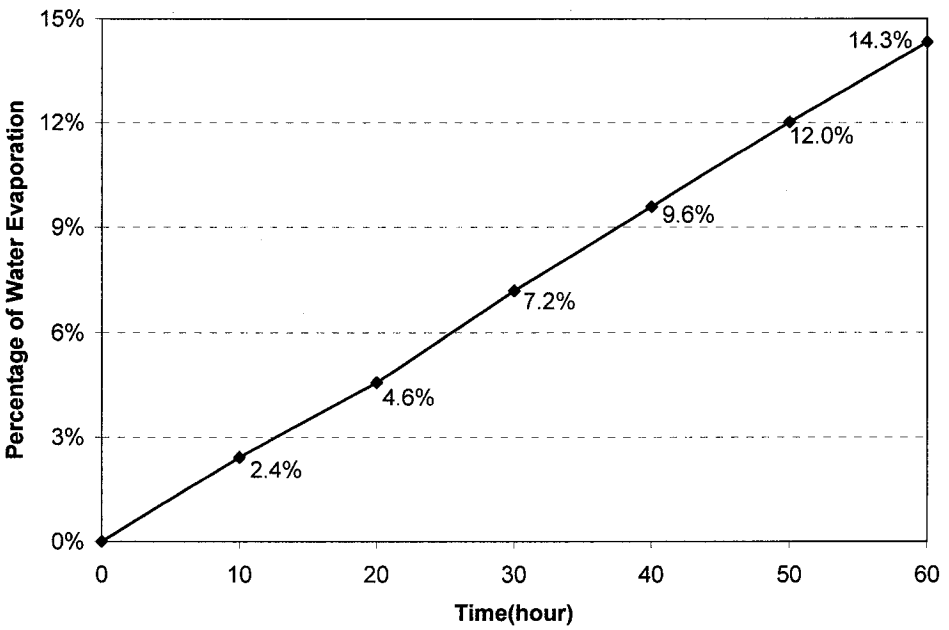


Figure 4. 30: Percentage of water evaporation during 1 hour oven-drying at 50°C for batch PC1HC

It can be seen that either 18 or 19 hour presetting open to air, led to significant water evaporation. Percentages of water loss for both two batches were on the order of 20%. It is indicated that presetting in air is effective to evaporate some amount of moisture. To make carbonation curing efficient, additional moisture should be driven out from precast

LWA concrete even after 18 hour presetting. Thereafter, gradual water evaporation was obtained through over-drying within 1 hour. The water to cement ratio of each batch prior to carbonation was summarized in Table 4.9. For precast LWA concrete, 36% water loss during presetting and oven-drying decreased water to cement ratio from 0.68 to 0.44. While for precast concrete with limestone, 23% moisture evaporation through presetting led to water to cement ratio from 0.48 to 0.37.

4.3.2 Carbonation Curing Behavior

Results for carbon dioxide absorption by precast concrete are presented in Table 4.10. The peak temperatures of the same batch were found to be in the same order and the minor difference might be attributed to experimental variation. For batch PC1, the surface temperature was around 30°C at the beginning of carbonation because they were heated by oven. As a result, the maximum temperature of the batch PC1 was over 10°C higher than that of batch PC2. Typical mass curves of concrete compacts and precast concrete were compared in Figure 4.31. Differing from concrete compacts of batch C3CB (limestone, w/c=0.26), carbon dioxide absorption of precast concrete of batch PC1 (LWA, w/c=0.44) was initially not that significant but continued to increase gradually at later age. Precast concrete in batch PC1 possessed slightly higher final mass gain through 2 hour carbonation than that of concrete compacts. Moreover, it could be predicted that a larger amount of carbon dioxide might be sequestered beyond 2 hours. A similar mass curve in carbonation curing to that observed with concrete compacts was found for the precast concrete samples in batch PC2 (limestone, w/c=0.37) but with lower carbon dioxide uptake. It was also observed that carbonation of samples in batch PC1 resulted in 3.8% and 4.5% higher water loss and carbon dioxide uptake respectively than those in batch PC2. It is indicated that potential carbon dioxide uptake can be effectively promoted by means of oven-drying to remove extra moisture from surface of fresh precast concrete.

Table 4. 10: Characteristics of carbonation for precast concrete

Batch	Carbonation (2hr) /hydration (28d)	Peak Temperature (^{O}C)	Water Loss[1] (%)	MG[2] (%)	MC[3] (%)	w/c after Carbonation
PC1	2 hr	53±1	10.5 ±0.6	11.7 ±1.0	12.3	0.39
	2 hr+28d					
PC2	2hr	39.5±0.5	6.7 ±0.6	7.2 ±0.2	7.4	0.35
	2 hr+28d					

Note:
1 Ratio of water evaporated to water content before carbonation
2 Percentage of weight gain calculated from Equation 3.3
3 Percentage of CO_2 mass gains from mass curve readings

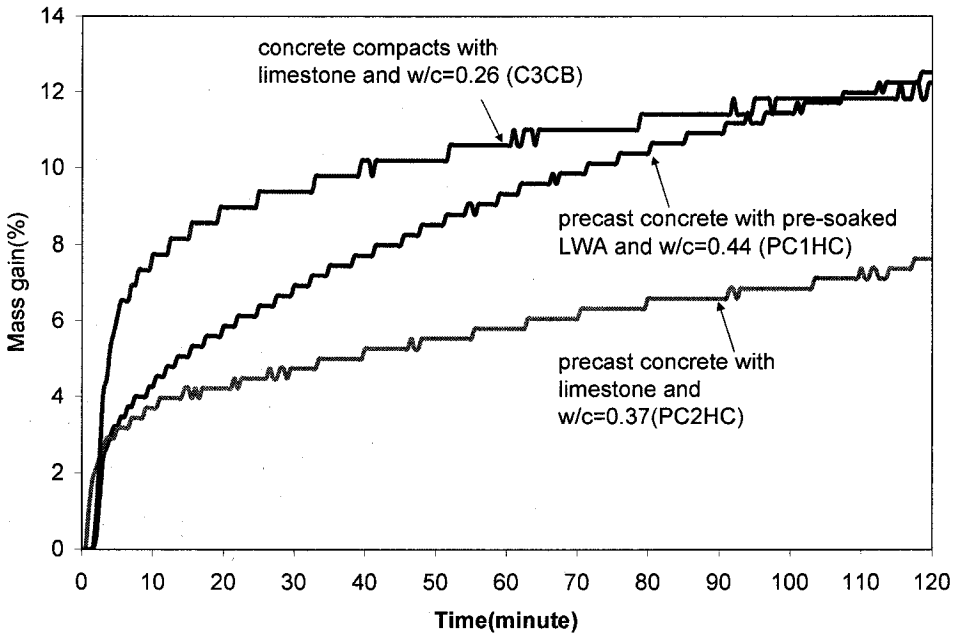


Figure 4. 31Typical mass curves of concrete compact and precast concrete during carbonation curing

4.3.3 Compressive Strength

Compressive strength testing results for precast concrete through 2 hour carbonation following 28 day hydration are displayed in Table 4.11. For both batches, early-age compressive strengths of precast concrete samples significantly increased through 2 hour carbonation, both of which exceeded that of conventionally hydrated samples at same age. Moreover, although weaker LWA was incorporated in samples of the batch PC1,

immediately carbonated samples possessed 15.0 MPa compressive strength, only 1.1 MPa lower than that of carbonated samples of batch PC2 with limestone. It should be noted that carbonation of samples in batch PC1 led to 4.48% higher weight gain than those in batch PC2. It was thus suggested that early-age compressive strength right after carbonation was dependent on quantity of carbon dioxide uptake.

Two hour carbonated samples in both batches doubled their compressive strengths in subsequent 27 day hydration. However, neither of them could exceed that developed in normal hydration at same age. In section 4.2.2.1, it was proposed that strength development of carbonated concrete compacts could be promoted by replacing partial limestone with pre-soaked LWA to act as an internal curing agent. Herein, it was found that, although certain content of moisture was provided by uniformly distributed LWA in the batch PC1, it did not help gain more compressive strength in batch PC2. This might have occurred because of a large amount of weaker component — LWA used in concrete that may have a detrimental effect on compressive strength, if compared to limestone concrete.

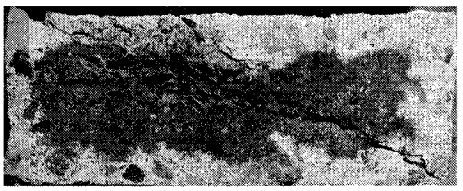
Table 4. 11: Compressive strength results for carbonated precast concrete up to 28-day hydration

Batch		Treatment	Age	Compressive Strength(MPa)
PC1	PC1H	21hr hydration in air	21hr	4.7±0.3
	PC1H28	21hr hydration in air +27d in moist room	28d	32.9±1.5
	PC1HC	18hr hydration in air +1hr dry+2hr carbonation	21hr	15.0±1.6
	PC1HC28	18hr hydration+1hr dry +2hr carb+27d in moist room	28d	30.8±0.4
PC2	PC2H	21hr hydration in air	21hr	9.8±0.8
	PC2H28	21hr hydration in air +27d in moist room	28d	36.1±0.8
	PC2HC	19hr hydration in air +2hr carbonation	21hr	16.8±0.6
	PC2HC28	19hr hydration+2hr carbonation+27d in moist room	28d	34.4±3.5

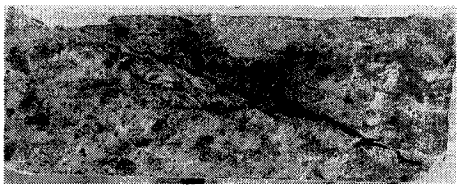
4.3.4 Qualitative Depth of Carbonation

Typical qualitative depth of carbonation patterns are illustrated in Figure 4.32 and Figure 4.33. For immediately carbonated samples of batch PC1 with about 11% carbon dioxide uptake, right after spraying indicator solution, there was a distinguishable colorless outermost surface surrounding an inner core region of purple. While, for carbonated samples in batch PC2 with only approximate 7% carbon dioxide absorption, almost no colorless region was able to be identified. Similar to concrete compacts, it appeared that the colorless region was dependent on the carbon dioxide uptake through carbonation curing. It was also observed that subsequent 28-day hydration in batch PC1 led to somewhat reduction of colorless area and the border between colorless and purple region became faint. For batch PC2, no remarkable difference could be found following further hydration at similar age. Some colorless spots still remained in the carbonated samples and the color pattern did not become purely purple as that of normally hydrated samples shown in Figure 4.34.

Similar to what was previously found in cement paste and concrete compacts, 24 hours after spraying phenolphthalein resulted in the faint border between previously colorless and purple zones. This finding might be attributed to further hydration in fresh precast concrete within 24 hours. It suggested that phenolphthalein test could not determine the nature of early-age carbonation on partially hydrated fresh precast concrete.

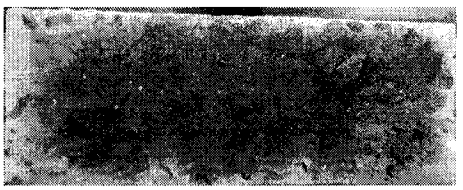


Immediately after spraying indicator solution

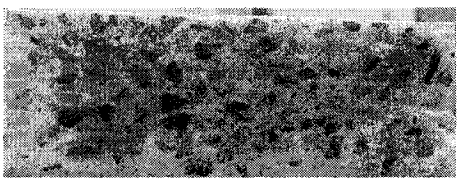


24 hours after spraying indicator solution

(a) Immediately after 2 hour carbonation (PC1HC)



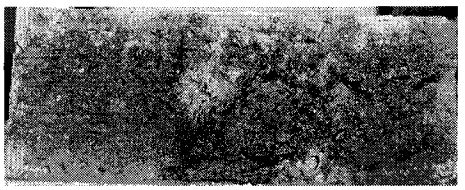
Immediately after spraying indicator solution



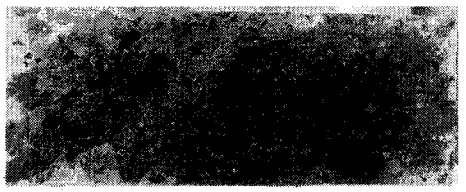
24 hours after spraying indicator solution

(b) After 2 hour carbonation and 28d hydration (PC1HC28)

Figure 4. 32: Qualitative depth of carbonation of pre-cast concrete after carbonation curing or/and hydration up to 28 days for batch PC1



(a) Immediately after 2 hour carbonation (PC2HC)



(b) After 2 hour carbonation and 28d hydration (PC2HC28)

Figure 4. 33: Qualitative depth of carbonation of pre-cast concrete after carbonation curing or/and hydration up to 28 days for batch PC2

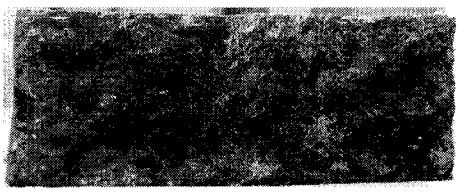


Figure 4. 34: Qualitative depth of carbonation of pre-cast concrete after 28 day hydration

4.3.5 pH of Pore Solution

pH results of precast concrete through 2 hour carbonation following 28-day hydration together with references of only hydration are presented in Table 4.12. pH values of the surface in batches PC1 and PC2 were reduced to 11.84 and 12.38 respectively, which depended on quantity of carbon dioxide uptake through carbonation curing. Core regions of concrete samples appeared not to be affected by early-age carbonation because pH in the core was very close to those of conventionally hydrated samples. Although cured in moist room for 28 days, carbonated concrete samples in both cases did not see any further pH restoration. It was found that early-age carbonation resulted in a pH reduction in fresh precast concrete. However pH still maintained at about 11.8 and above. As long as controlled carbonation curing is able to ensure pH values greater than 11.5, carbonation-initiated corrosion might be inhibited. After 28-day moist hydration, the stabilization of pH in both surface and core of carbonated concrete indicated carbonated surface could be achieved with little effect on the core through controlled early age carbonation. Therefore, carbonation curing could be used in precast concrete with reinforcing steel. Furthermore, the diffusion resistance would improved by densified surface to prevent weathering carbonation in service (Sanjuán and Olmo 2001).

Table 4. 12: pH results for carbonated precast concrete up to 28 day hydration

Batch		Treatment	Age	pH		
				Bulk	Surface	core
PC1	PC1H	21hr hydration in air	21hr	12.72	/	/
	PC1H28	21hr hydration in air +27d in moist room	28d	12.70	/	/
	PC1HC	18hr hydration in air +1hr dry+2hr carbonation	21hr	/	11.84	12.68
	PC1HC28	18hr hydration+1hr dry+2hr carbonation+27d in moist room	28d	/	11.88	12.71
PC2	PC2H	21hr hydration in air	21hr	12.74	/	/
	PC2H28	21hr hydration in air +27d in moist room	28d	12.72	/	/
	PC2HC	19hr hydration in air +2hr carbonation	21hr	/	12.38	12.68
	PC2HC28	19hr hydration+2hr carbonation+27d in moist room	28d	/	12.36	12.67

4.3.6 X-ray Diffraction

The products formed after 2 hour carbonation and following hydration were examined through x-ray diffraction analysis on precast concrete samples of the batch PC1 (pre-soaked LWA). The XRD patterns of carbonated samples are displayed in Figures 4.35. It was shown that calcite was the main form of calcium carbonate after early age carbonation and aragonite was only weakly detected in the core. XRD patterns revealed calcium carbonate of medium strong intensity and SiO_2 of very strong intensity. Remarkable discrepancy was observed in XRD spectra between the surface and core samples through 2 hour carbonation curing. Hydrated phase, such as calcium hydroxide was not found in the surface sample right after carbon dioxide treatment; while in the core, XRD spectra revealed several calcium hydroxide peaks with three strongest at 18.1°, 34.2° and 47.1°. Some previous findings can be verified through XRD analysis. On the one hand, prediction of further increase of carbon dioxide uptake beyond 2 hour exposure for the batch PC1 was consistent with the fact that calcium hydroxide was not entirely depleted during 2 hour. On the other hand, the results on significant difference of pH values between the surface and the core might be confirmed with this observation. After 2 hour carbonation curing following 27 day hydration in moist room, no remarkable difference was observed for both surface and the core samples. Very weak ettringite lines could be detected after subsequent 27 day hydration for both the surface and core samples. It was consistent with the finding that pH values of carbonated samples changed little during the subsequent hydration.

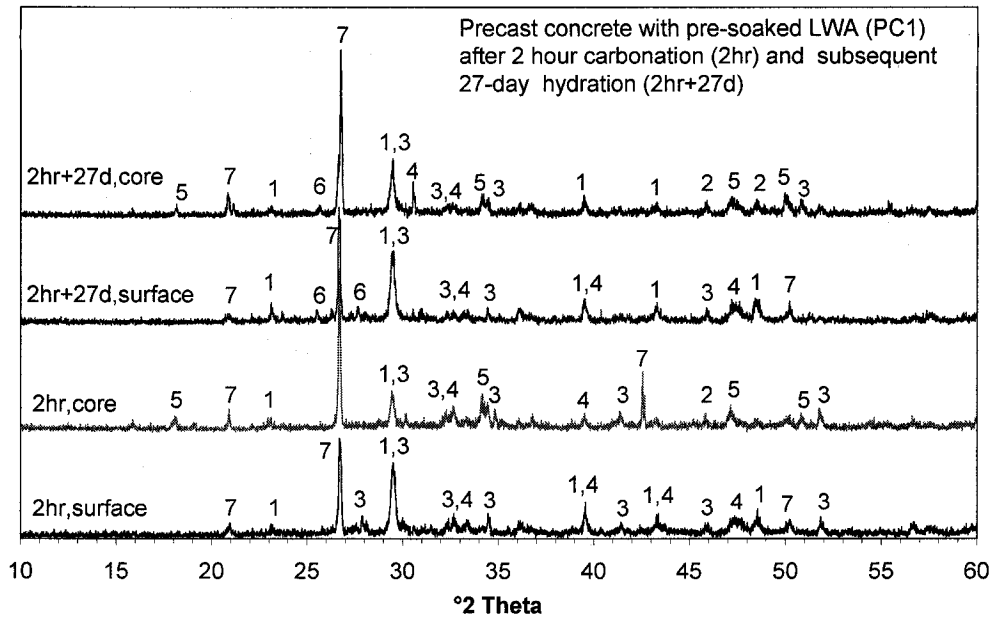


Figure 4. 35: X-ray diffraction diagrams of precast concrete (PC1) after 2 hour carbonation following 28 day hydration: (1) calcite, (2) aragonite, (3) C_3S, (4) C_2S, (5) calcium hydroxide, (6) ettringite, (7) SiO_2

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

Carbon dioxide absorption and properties of carbonated concrete at later age were studied to investigate feasibility of carbon dioxide sequestration through carbonation curing of cement-based products. Cement paste compacts were used to better understand the mechanism and effect of early-age carbonation curing, concrete compacts to simulate concrete blocks or pavers and precast to explore new candidate products that can serve carbon dioxide capture and storage and simultaneously achieve beneficial properties. Cement paste compacts, concrete compacts and precast concrete samples were examined to quantify carbon dioxide uptake, mechanical performance and pH values as a result of carbonation curing. Qualitative depth of carbonation was also studied on all three typical products.

5.1.1 Performance of Carbonated Cement Paste and Concrete Compacts

From assessment of carbon dioxide absorption, flexural and compressive strengths, and pH values in carbonated cement paste and concrete compacts, the following conclusions are drawn:

1) Batch size significantly influenced peak temperature and water loss, while it had a negligible effect on the quantity of carbon dioxide absorbed. Various gas pressure levels (0.5 MPa/0.15 MPa) led to some discrepancies in peak temperature and water loss and had no remarkable effect on carbon dioxide uptake. Shortening the duration of carbonation decreased quantity of water loss and amount of carbon dioxide uptake. Even if treated with the moisturized carbon dioxide gas for 4 days, fresh cement paste samples were unable to sequester much more carbon dioxide to achieve full carbonation.

2) Trends of carbonation behaviour were similar in cement paste and concrete compacts. For concrete samples, the maximum temperature and amount of water loss were lower than those for cement paste compacts due to low cement content in concrete compacts. For both cement paste and concrete compacts, the quantity of carbon dioxide absorption was proportional to percentage of water loss during carbonation reaction.
3) The quantity of carbon dioxide absorbed in cement paste compacts was about 13% after 2 hour carbonation, 3% higher than that of concrete compacts (without any internal curing agent). 0.1% starch-based chemical admixture incorporating in concrete samples could not help reduce water loss during carbonation reaction but did promote carbon dioxide uptake by over 1.2%.
4) Gas pressure had no significant effect on early-age flexural strength of cement paste samples but had remarkable influence on further flexural strength development in subsequent hydration. Subsequent hydration following 2 hour carbonation wouldn't improve flexural strengths of carbonated samples whether cured in water or in sealed bags.
5) After carbonation at 0.15 MPa within 2 hours, 1 hour and 30 minutes, initial flexural strengths were dependent on contents of carbon dioxide absorbed by cement paste compacts, and they significantly decreased at later age. 1 hour exposure resulted in maximum flexural strength up to 28 days. Prolonged carbonation for 4 days with moisturized carbon dioxide gas could gain additional flexural strength as a result of higher carbon dioxide uptake.
6) 28-day flexural strengths of carbonated cement paste samples significantly exceeded those of their hydrated references at same age.
7) Gas pressure effect was negligible on compressive strengths of carbonated cement paste compacts. Compressive strengths of 2-hour carbonated samples were not significantly improved in subsequent hydration whether cured in water or in sealed bags.
8) Early-age compressive strength was dependent on the quantity of carbon dioxide absorbed by cement paste samples within 2 hours. Although maximum 28-day compressive strength could be achieved through 1 hour treatment, while it was

unable to be compared with that developed in conventional hydration. It was predicted that 30-minute carbonated samples with lowest strength at early age, would achieve the highest compressive strength in the long term. Continuous carbonation for 4 days did not make special contribution to compressive strength gain.

9) Carbonated cement paste samples cured in sealed bags for 28 days possessed higher compressive strength than that of hydrated samples at same age. While compressive strength of non-carbonated samples cured in water exceeded that of carbonated samples up to 28 days.
10) Higher early-age flexural and compressive strengths of carbonated cement paste samples did not have subsequent hydration strength in proportion up to 28 days. The carbon dioxide uptake and water loss in carbonation reaction might be considered as two influencing factors on strength development in subsequent hydration. Carbonation curing could be controlled to sequester certain amount of carbon dioxide with desired long-term mechanical properties.
11) Similar to cement paste samples, 2-hour carbonated concrete compacts (without treatment) experienced a reduction in flexural strength throughout subsequent hydration, while compressive strength was improved to certain level up to 28 days. Both flexural and compressive strengths of conventionally hydrated samples (without treatment) exceeded those of 2-hour carbonated specimens following 28 day hydration.
12) Internal curing was an effective way to enhance strength development for carbonated concrete samples in the long term. By using pre-soaked LWA, both flexural and compressive strengths of carbonated samples exceeded those of hydrated samples up to 28 days, because pre-soaked LWA acted as the uniformly distributed water resource to help achieve better hydration.
13) Starch-based chemical admixture of 0.1% dosage might not have significant effect on both early-age flexural and compressive strengths through carbonation curing, however its contribution to 28-day strengths could be very remarkable exceeding that of hydrated concrete samples at same age. High dosage of this type of chemical admixture was detrimental

14) Phenolphthalein solution indicator may not be suitable for predicting depth of carbonation for fresh cementitous products and assessing effect of early-age carbonation.

15) pH values of the surface layer were reduced to around 12.0 immediately after 2 hour carbonation, and those in the core were observed to be slightly higher.

16) Gas pressure effect was not noticeable on pH assessment. 28-day subsequent hydration either in water or in sealed bags was unable to significantly restore the pH value. Carbonated samples, which were cured in tap water for better hydration, possessed only slightly higher pH values than those of carbonated samples hydrated in sealed bags.

17) pH values of immediately carbonated cement paste samples were dependent on quantity of carbon dioxide absorbed through carbonation curing. They were restored to various degrees up to 28-day hydration for both surface and core. For carbonation at both 1 hour and 30 minutes, pH values of the core could be compared with that of normally hydrated samples. Prolonged treatment with carbon dioxide for continuous 4 days did not lead to much decreased pH value due to a slightly more carbon dioxide uptake and simultaneous hydration in moist environment.

18) pH values of carbonated cement paste samples were reduced but they were still greater than 11.5 to safeguard the passive film and thus inhibit corrosion. Similar behaviour was found in concrete compacts. It is also suggested that the pH values of carbonated cement-based products could be controlled by varying duration of carbonation curing.

19) Calcium carbonates in the form of calcite and aragonite were the primary products after 2 hour carbonation curing and hydration products were not revealed. Further 28 day hydration produced somewhat but not sufficient hydration products, such as calcium hydroxide and ettringite. It is suggested that later-age hydration could be retarded or impeded through carbon dioxide treatment.

5.1.2 Properties of Precast Concrete

20) Water content is a critical parameter influencing carbonation curing of fresh precast concrete. Certain amount of moisture should be removed from samples by means of presetting and oven-drying so that carbonation curing is possible. Moreover, carbon dioxide absorption can be effectively promoted through oven-drying. Water evaporation should be monitored during these two processes prior to treatment with carbon dioxide.

21) Early age compressive strength precast concrete samples after 2 hour carbonation remarkably exceeded that of their reference at same age. Similar to cement paste and concrete compacts, initial strength appeared to be dependent on quantity of carbon dioxide absorbed by precast concrete samples.

22) 2 hour carbonated samples doubled their compressive strengths in subsequent 28 day hydration, but did not possessed higher results than that developed for conventional hydration at same age.

23) Phenolphthalein test might not be appropriate to identify the nature of early age carbonation on fresh precast concrete.

24) pH reduction of the surface was dependent on amount of carbon dioxide absorbed by precast concrete. In each case, the core seemed not to be affected by carbonation curing so that pH approximated that of normally hydrated samples. pH restoration was not observed and pH appeared to be stabilized in carbonated samples after subsequent 28 day hydration in moist room.

25) Similar to findings in cement paste cement compacts, calcium carbonates in the form of calcite and aragonite were the primary products after 2 hour carbonation curing. Hydrated compounds were not detected in the surface sample, while were observed in the core. This might confirm two findings of further carbon dioxide absorption beyond 2 hours and very high pH in the core. Further 28 day hydration had little influence on pH restoration of both surface and the core.

5.2 Recommendations for Future Work

The following items should be required for further study:

1) Investigation into long term mechanical performance of carbonated cement-based products with and without treatment of internal curing agent or chemical admixture — Solvitose FC 100.
2) Optimization on carbonation curing of precast concrete, varying parameters such water to cement ratio, duration of presetting and oven-drying, and carbonation time.
3) Investigation into effect of presetting drying on shrinkage of precast concrete.
4) Investigation into "controlled carbonation" of concrete products to sequester carbon dioxide and simultaneously achieve desired properties.

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Appendix A: Experimental Data of Cement Paste Compacts

Appendix A.1: Carbonation curing behavior of cement paste compacts

Batch	CO_2 Gas Pressure (MPa)	Carbonation Curing Duration (hr)	Peak Temperature (°C)	Initial Mass (g)	Mass After Carbonation (g)	Weight of Collected Water (g)	Water Loss (%)	MG* (%)	MC** (%)
P1C	0.5	2	81	274.0/273.5	291.8/291.8	21.8	30.53	12.16	13.46
P2CB	0.5	2	119	271.6/272.9/ 272.7/272.8/ 272.8/272.7	284.7/285.7/ 286.6/286.0 286.6/286.8	100.2	46.98	12.77	14.11
P3CB	0.15	2	107	272.5/273.3/ 272.8/272.8/ 272.6/373.2	283.4/283.6/ 283.3/282.7/ 282.5/284.7	118.6	55.54	12.76	15.87
P4CW	0.5	2	118	272.6/272.7/ 271.6/272.3/ 271.2/271.1	288.0/286.9/ 285.2/286.3 284.6/285.7	107.6	50.56	13.59	15.68
P5CW	0.15	2	112	271.9/272.2/ 272.2/272.2/ 272.4/272.6	282.8/281.8/ 283.0/281.9/ 283.6/286.1	115.2	54.07	12.74	13.82
P6C	0.15	96	103	270.7/271.0/ 271.6/272.0/ 272.6/273.6	292.0/290.3/ 292.3/292.1/ 294.4/294.9	/	/	/	14.68
P7CW	0.15	1	101	272.6/272.4/ 272.7/272.7/ 272.8/272.6	281.3/280.6/ 285.9/281.8/ 280.9/285.3	99.1	46.45	11.19	12.11
P8CW	0.15	0.5	100	272.7/272.7/ 272.2/272.7/ 272.6/272.7	278.2/277.4/ 275.5/275.8/ 277.1/278.1	75.6	35.44	7.18	8.74

P=cement paste compact, C=carbonation, B=subsequent hydration in sealed bags, W=subsequent hydration in water
MG*=weight gain determined from Equation 3.6; MC**=CO_2 uptake by mass curve readings

Appendix A.2: Mechanical performance and pH of carbonated and hydrated cement paste compacts

Batch		Geometry (mm*mm*mm)	Mechanical Testing		pH	
			MOR (MPa)	fc'(MPa)	Surface	Core
P2CB	P2CB0*	127.3*76.4*14.4/ 127.3*76.4*14.5	9.3/8.9	55.3/53.0	12.06	12.22
	P2CB4**	127.5*76.4*14.3/ 127.5*76.3*14.2	8.0/11.3	55.8/47.6	12.09	12.24
	P2CB28***	127.9*76.2*14.5/ 127.5*76.4*14.6	9.8/8.8	57.1/48.4	12.18	12.30
P3CB	P3CB0	127.3*76.4*14.5/ 127.3*76.4*14.5	9.4/10.1	58.3/59.9	12.01	12.06
	P3CB4	127.4*76.2*14.6/ 127.2*76.3*14.6	8.2/8.0	58.1/61.7	12.07	12.09
	P3CB28	127.8*76.6*14.4/ 127.9*76.9*14.5	10.6/6.3	65.5/59.1	12.20	12.22
P4CW	P4CW0	127.8*76.6*14.4/ 127.9*76.9*14.5	9.3/9.9	56.4/46.2	11.97	12.27
	P4CW4	127.8*76.3*14.4/ 127.4*76.5*14.4	10.0/9.9	59.1/60.5	12.14	12.36
	P4CW28	128.2*76.7*14.4/ 128.2*76.8*14.2	8.7/10.6	58.4/49.4	12.23	12.38
P5CW	P5CW0	127.4*76.4*14.2/ 127.5*76.4*14.3	9.4/10.1	58.3/59.9	11.98	12.14
	P5CW4	127.6*76.4*14.4/ 127.8*76.4*14.3	7.4/9.3	60.9/60.7	12.10	12.27
	P5CW28	127.7*76.3*14.7/ 127.6*76.5*14.8	9.3/6.2	56.9/54.3	12.26	12.38

P=cement paste compact, C=carbonation, B=subsequent hydration in sealed bags, W=subsequent hydration in water
0*=at age of 0 day; 4**=at age of 4 days; 28***=at age of 28 days

Appendix A.3: Mechanical performance and pH of carbonated and hydrated cement paste compacts (cont'd)

Batch		Geometry (mm*mm*mm)	Mechanical Testing		pH	
			MOR (MPa)	fc'(MPa)	Surface	Core
P6C	P6C0	127.3*76.3*14.2/ 127.3*76.4*14.3	9.7/11.3	58.6/57.9	11.99	12.21
P7CW	P7CW0	127.3*76.4*14.4/ 127.3*76.4*14.5	7.9/10.1	55.0/56.2	12.15	12.37
	P7CW4	127.5*76.4*14.3/ 127.5*76.3*14.2	9.8/7.5	53.9/54.5	12.23	12.51
	P7CW28	127.9*76.2*14.5/ 127.5*76.4*14.6	9.1/6.7	78.9/70.2	12.36	12.69
P8CW	P8CW0	127.3*76.4*14.5/ 127.3*76.4*14.5	6.7/7.2	37.3/35.2	12.26	12.60
	P8CW4	127.4*76.2*14.6/ 127.2*76.3*14.6	6.8/5.7	43.0/56.6	12.26	12.63
	P8CW28	127.8*76.6*14.4/ 127.9*76.9*14.5	4.3/4.9	64.1/65.1	12.39	12.71
P9HW	P9HW4	127.8*76.6*14.4/ 127.9*76.9*14.5	2.8/3.3	47.1/45.3	12.58	
	P9HW28	128.2*76.7*14.4/ 128.2*76.8*14.2	2.8/2.4	82.2/85.5	12.70	
P10HB	P10HB4	127.7*76.5*14.6/ 127.6*76.7*14.3	3.6/2.0	36.8/47.2	12.70	
	P10HB28	128.8*76.7*14.3/ 128.8*76.5*14.6	4.2/3.2	39.3/38.3	12.72	

P=cement paste compact, C=carbonation, H=hydration
B=subsequent hydration in sealed bags, W=subsequent hydration in water
0*=at age of 0 day; 4**=at age of 4 days; 28***=at age of 28 days

Appendix A.4: Data of constant-temperature pyrolysis techniques for cement paste compacts

Sample		105°C LOI (%)	500°C LOI (%)	1000°C LOI (%)	Total LOI (%)	CO_2 Content (%)
P1C0	surface	1.94	4.32	10.48	16.75	11.94
	core	3.16	3.44	10.37	16.97	11.84
P2CB0	surface	1.56	4.09	10.49	16.13	11.86
	core	2.33	3.34	12.14	17.81	14.11
P3CB0	surface	1.79	3.97	10.52	16.28	11.92
	core	2.36	3.44	13.37	19.17	15.87
P4CW0	surface	1.49	4.22	11.31	17.02	12.98
	core	2.10	3.60	13.25	18.95	15.68
P5CW0	surface	2.06	3.94	11.12	17.12	12.77
	core	2.50	3.67	11.81	17.98	13.74
P6C0	surface	2.21	4.39	11.94	18.55	14.00
	core	2.44	4.01	13.38	19.83	16.02
P7CW0	surface	1.96	4.42	10.16	16.54	11.53
	core	2.26	3.43	9.39	15.08	10.42
P8CW0	surface	1.95	3.73	10.20	15.87	11.48
	core	2.16	2.82	7.55	12.53	8.01

Note:
Approximately 1g of each sample was ignited at 105°C, 500°C and 1000°C for 1 hour

Appendix B: Experimental Data of Concrete Compacts

Appendix B.1: Carbonation curing behavior of concrete compacts

Batch	CO_2 Gas Pressure (MPa)	Carbonation Curing Duration (hr)	Peak Temperature (°C)	Initial Mass (g)	Mass After Carbonation (g)	Weight of Collected Water (g)	Water Loss (%)	MG* (%)	MC** (%)
$C^1$3C^2B	0.15	2	54	430.5/430.7/ 431.0/431.0/ 429.1/428.8	433.2/433.5/ 433.7/433.0 432.1/432.2	30.6	23.71	9.62	11.89
C4CB	0.15	2	60	396.1/396.1/ 396.2/396.3/ 396.4/396.0	399.5/399.1/ 399.9/399.4/ 400.5/399.7	35.3	28.02	11.55	13.61
C5CB	0.15	2	53	400.6/400.9/ 401.3/400.8/ 400.7/401.2	402.9/403.0/ 403.7/432.5/ 403.0/403.3	29.2	18.68	8.62	10.30
C6CB	0.15	2	56	430.5/430.4/ 429.8/431.3/ 431.7/431.7	433.6/433.1/ 433.0/435.0/ 435.1/434.0	31.6	24.95	10.39	13.09
C7CB	0.15	2	56	430.0/430.2/ 429.7/429.4/ 429.4/425.3	435.0/434.0/ 434.3/434.8/ 435.5/428.5	31.2	24.72	11.77	13.62

C^1=concrete compact, C^2=carbonation, B=subsequent hydration in sealed bags
MG*=weight gain determined from Equation 3.6; MC**=CO_2 uptake recorded by mass curve

Appendix B.2: Mechanical performance and pH of carbonated and hydrated concrete compacts

Batch		Geometry (mm*mm*mm)	Mechanical Testing		pH
			MOR (MPa)	fc'(MPa)	Bulk
C1HB	C1HB28	127.4*76.4*20.4/127.6*76.5*20.3/ 127.5*76.4*20.4	1.9/1.8/1.9	16.4/16.0/16.3	12.81
C2HB	C2HB28	127.4*76.5*20.2/127.4*76.3*20.1/ 127.4*76.4*20.2	2.4/2.0/2.7	12.4/13.1/15.1	12.80
$C^1$3C^2B	C3CB0*	127.4*76.3*20.4/127.6*76.5*20.3/ 127.3*76.4*20.4	1.8/1.5/2.3	8.9/10.0/10.2	11.98
	C3CB28**	127.3*76.6*20.1/127.5*76.4*20.3/ 127.4*76.4*20.2	1.4/0.9/1.2	13.3/14.1/12.8	12.21
C4CB	C4CB0	127.4*76.3*20.1/127.3*76.4*20.3/ 127.3*76.5*20.1	2.0/1.9/2.0	8.1/8.1/7.7	11.86
	C4CB28	127.4*76.4*20.1/127.2*76.3*20.1/ 127.4*76.4*20.1	3.9/4.6/3.7	14.2/16.3/14.1	12.15
C5CB	C5CB0	127.5*76.4*20.3/127.4*76.5*20.2/ 127.4*76.5*20.3	1.5/1.4/1.5	7.4/7.6/6.7	12.18
	C5CB28	127.3*76.3*20.2/127.3*76.4*20.2/ 127.2*76.2*20.3	2.6/2.9/2.7	15.0/16.2/15.1	12.22
C6CB	C6CB0	127.8*76.4*20.3/127.6*76.6*20.3/ 127.6*76.6*20.4	1.8/1.5/1.2	9.5/9.6/9.7	12.01
	C6CB28	127.3*76.5*20.5/127.2*76.4*20.6/ 127.3*76.4*20.4	4.0/3.7/3.9	17.5/16.0/15.5	12.16
C7CB	C7CB0	127.8*76.6*20.7/128.0*76.8*20.9/ 128.1*76.8*20.9	0.9/1.0/0.6	5.8/6.2/4.8	11.80
	C7CB28	127.6*76.6*20.5/127.9*76.8*20.6/ 127.9*76.7*20.6	1.8/1.2/1.0	10.8/10.3/11.3	11.92

C^1=concrete compact, C^2=carbonation, H=hydration, B=subsequent hydration in sealed bags
0*=at age of 0 day; 28**=at age of 28 days

Appendix C: Experimental Data of Precast Concrete Samples

Appendix C.1: Water loss during 1-hour oven-dry at 50°C for precast concrete batch PC1

Batch	Sample	Time (minute)						
		0	10	20	30	40	50	60
PC1HC	1	547.3	544.5	541.7	538.9	536.8	535.0	533.1
	2	562.9	561.7	560.1	558.0	556.0	553.9	552.1
	3	568.8	567.5	565.6	563.3	561.2	559.0	556.9
	4	563.6	562.0	560.2	558.2	556.4	554.0	551.8
	5	539.7	537.9	535.9	533.9	531.9	529.8	527.8
	6	536.0	533.7	531.4	529.2	527.1	525.2	523.4
PC1HC28	1	543.8	541.5	539.1	536.7	534.5	532.6	530.9
	2	555.6	552.9	549.8	547.2	544.9	542.9	541.1
	3	559.0	557.1	554.2	551.9	549.8	548.0	546.2
	4	544.2	542.0	539.3	537.0	534.9	533.0	531.5
	5	550.1	547.8	545.3	543.1	541.4	539.7	538.2
	6	536.6	533.8	531.4	529.2	527.4	526.0	524.6

PC=precast concrete, H=hydration during presetting, C=carbonation, 28= at age of 28 days

Appendix C.2: Carbonation curing behavior of precast concrete batches

Batch		Carbonation Curing	Peak Temperature (°C)	Mass Before Carbonation(g)	Mass After Carbonation (g)	Weight of Collected Water (g)	Water Loss (%)	MG* (%)	MC** (%)
PC1	PC1HC	2 hour, 0.15 MPa	54	533.1/552.1/ 556.9/551.8/ 527.8/523.4	542.2/559.3/ 563.3/557.8/ 534.6/532.0	36.3	23.71	10.71	12.31
	PC1HC28	2 hour, 0.15 MPa	53	530.9/541.1 546.2/531.5/ 538.2/524.6	540.1/551.0/ 555.6/541.6/ 550.1/536.6	31.6	28.02	12.64	/
PC2	PC2HC	2 hour, 0.15 MPa	39	690.0/677.9/ 664.6/672.6/ 672.7/706.6	696.8/684.7/ 670.3/677.9/ 678.7/710.9	17.3	18.68	7.04	7.44
	PC2HC28	2 hour, 0.15 MPa	40	691.0/671.7/ 657.2/663.7/ 654.5/676.3	695.7/677.5/ 663.3/669.6/ 660.3/682.7	20.2	24.95	7.36	/

PC=precast concrete, H=hydration during presetting, C=carbonation, 28= at age of 28 days
MG*=weight gain determined from Equation 3.6, MC**=CO_2 uptake recorded by mass curve

Appendix C.3: Mechanical performance and pH of carbonated and hydrated precast concrete batches

Batch		Geometry (mm*mm*mm)	Mechanical Testing fc'(MPa)	pH	
				Surface	Core
PC1	PC1H	128.5*77.1*30.1/128.4*76.6*30.2/ 128.3*76.5*30.4	4.1/4.6/4.4	12.72	
	PC1H28	127.2*76.3*30.6/127.8*76.6*29.6/ 127.9*76.7*29.6	30.6/31.2/30.6	12.70	
	PC1HC	127.7*76.8*30.4/128.3*76.7*31.3/ 128.7*76.6*31.5	14.2/16.8/14.0	11.84	12.68
	PC1HC28	127.1*76.7*31.0/127.0*76.5*30.7/ 126.4*76.8*30.6	34.5/31.5/32.6	11.88	12.71
PC2	PC2H	128.6*77.0*33.0/128.5*76.7*32.1/ 128.6*76.6*31.8	10.5/8.9/9.9	12.74	
	PC2H28	129.5*76.6*31.5/129.6*76.8*31.6/ 129.0*76.6*29.6	36.8/35.2/36.4	12.72	
	PC2HC	127.6*76.8*30.8/128.1*76.5*30.5/ 128.2*76.6*30.3	16.3/16.6/17.5	12.38	12.36
	PC2HC28	126.8*76.9*30.8/127.1*76.7*30.8/ 127.7*76.5*30.5	38.4/32.3/32.5	12.68	12.67

PC=precast concrete, H=hydration during presetting, C=carbonation, 28= at age of 28 days